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# Mono- and di-nuclear nickel(II) complexes with mixed N/S-donor ligands: Syntheses, structures and physical properties

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ABSTRACT

Two new Ni(II) complexes are reported with tridentate thiosemicarbazone ligands derived from Schiff-base condensation with phenylthiosemicarbazide. Complex **1**, a novel dinuclear Ni(II) complex of a SNS ligand synthesized by reaction with 2,2′-dithiodibenzaldehyde (DTDB), adopts a butterfly-type structure in which thiolates derived from DTDB reside in the bridging positions. Complex **2**-$(NO_3)_2$, a mononuclear Ni(II) complex of a NNS ligand synthesized by reaction with pyridine carboxaldehyde features two ligands spanning three meridional positions on the pseudo-octahedral coordination sphere of the Ni(II) center. The thiosemicarbazone-S is coordinated to the Ni(II) center in **1** in the deprotonated anionic thiolate-S form, while the neutral thione-S is present in **2**-$(NO_3)_2$. To the best of our knowledge complex **1** is the first example of a dinuclear bis(thiolate)-bridged Ni(II) complex with $NS_3$ coordination involving a thiosemicarbazide moiety.



## 1. Introduction

Interest in the bioinorganic chemistry of nickel has increased recently, with the discovery of two new metalloenzymes which contain Ni at their active sites, bringing to six the number of established Ni-containing enzymes [1]. The two most recently discovered are redox-active enzymes with Ni coordination spheres involving N- and S-donors. Ni superoxide dismutase (NiSOD) has an active-site Ni coordinated by an amine-N, an amide-N and two thiolate-S donors, and catalyzes the disproportionation of superoxide into hydrogen peroxide and molecular oxygen [2–4]. The A-cluster of carbon monoxide dehydrogenase/acetyl coenzyme-A synthase (CODH/ACS) catalyzes the assembly of acetyl CoA [5,6]. It features an Fe–S cubane bridged through a thiolate-S atom to an asymmetric dinuclear Ni cluster. The proximal Ni ($Ni_p$), in addition to the thiolate-S bridging it to the Fe, is coordinated by an unidentified exogenous N or O donor ligand and two thiolate-S atoms bridging it to the distal Ni ($Ni_d$). The coordination sphere of $Ni_d$ is completed by two amide-N donors [7–9]. While the chemistry of Ni complexes with mixed N/S coordination spheres has been an active research area for many decades, it has become more significant as researchers endeavor to use synthetic analogs of the enzyme active sites to understand their unique reactivities. A common feature in redox active nickel enzymes is the presence of thiolate coordination, which, along with other structural features, is implicated in helping the nickel center to access different oxidation states during the catalytic cycle. While much research effort has been expended on physical and biochemical studies of these enzymes, full understanding of how the different ligand environments facilitate the catalysis of these reactions does not yet exist. In particular, the unusual donor sets must tune the potential of the Ni center, making it important to understand the effect of the component ligands on the reduction potential.

The synthesis of metal complexes with thiolate coordination is often complicated by the oxidative sensitivity of the thiol. Hahn and coworkers have recently reported the template synthesis of thiolate-containing Schiff base complexes using a preformed complex of 2-thiolatobenzaldehyde [10]. We have been developing, for the past decade, a methodology for the synthesis of metal complexes with mixed N/S donation using 2,2′-dithiodibenzaldehyde (DTDB) as an air-stable reactant to provide thiolate donation without relying on cumbersome protection and deprotection of the thiolate [11]. This methodology involves the reaction of DTDB with metal complexes containing coordinated primary amines, resulting in Schiff-base condensation with the aldehyde functionality of DTDB and concomitant cleavage of the disulfide to provide the thiolate donor. Among the complexes we have reported using this methodology are (i) symmetric bis(thiolate)-bridged Ni dimers formed by the reaction of DTDB with $Ni(aet)_2$ (Haet = 2-aminoethanethiol) or $Ni(ma)_2$ (Hma = 2-mercaptoaniline) in which both Ni atoms in the dimers have $NS_3$ coordination environments [12],

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reminiscent of $Ni_p$ in CODH/ACS and (ii) a mononuclear complex with Ni coordinated by an amine-N, an imine-N and two thiolate-S atoms which is reminiscent of the Ni coordination environment in NiSOD [13].

Thiosemicarbazone ligands, derived from the combination of a thiosemicarbazide and an aldehyde or ketone, are another useful ligand type for obtaining coordination spheres with mixed N/S donors. Interest in these ligands has been driven, in part, by potentially beneficial biological activity of the ligands and their metal complexes, including antitumor, fungicidal, bactericidal and antiviral activity [14,15]. We have reported Fe(III) and Co(III) complexes of bis(thiosemicarbazone) ligands resulting from Schiff-base condensation of 2,6-diacetylpyridine with thiosemicarbazides [16]. As part of our long-standing interest in synthesizing model complexes for the active sites of metalloenzymes with mixed N/S coordination spheres we report herein a dinuclear Ni(II) complex of a thiosemicarbazone ligand synthesized by the reaction of DTDB with phenylthiosemicarbazide, as well as a mononuclear Ni(II) complex of a ligand derived from pyridine carboxaldehyde and phenylthiosemicarbazide.

## 2. Experimental

### 2.1. General

All chemicals and solvents were reagent grade and were used as received from Aldrich, Acros and Fisher Scientific. 2,2′-Dithiodibenzaldehyde was synthesized by literature methods [17,18]. Elemental analyses for C, H and N were conducted using the Pregl–Dumas technique on a Thermo Fischer Flash EA1112 analyzer. FT-IR spectra were recorded as KBr pellets in the 400–4000 $cm^{-1}$ range on a Nicolet 750 Magna-IR spectrometer. UV–Vis data was collected on a Hitachi U-2010 spectrophotometer. Electrochemical data was collected on an EG&G Princeton Applied Research potentiostat model 263A with a Pt working electrode, Pt counter electrode and Ag/AgCl reference electrode.

### 2.2. Synthesis of complex [Ni(tp-pts)]$_2$ (**1**)

A solution of 2,2′-dithiodibenzaldehyde (135 mg, 0.5 mmol) in 50 mL of methanol was added drop wise to a solution of phenylthiosemicarbazide (167 mg, 1.0 mmol) in 30 mL of methanol. The solution was heated at reflux for 45 min, giving rise to an orange solution. Upon addition of $Ni(NO_3)_2{\cdot}6H_2O$ (290 mg, 1.0 mmol) in 20 mL of methanol, the solution immediately turned red and the mixture was then heated at reflux for 30 min. The solution was concentrated by rotary evaporation to ca. 10 mL, resulting in a precipitate, which was washed with a mixture of methanol/$Et_2O$ to give **1** as a purple crystalline solid. X-ray quality crystals were obtained by slow evaporation of a methanol solution over one week. Yield 290 mg, (0.42 mmol, 84%). Elem. *Anal.* Calc. for $C_{28}H_{22}N_6Ni_2S_4$: C, 48.89; H, 3.22; N, 12.22. Found: C, 48.99; H, 3.32; N, 12.09%. IR (KBr, $cm^{-1}$): 3195 w ($\nu_{NH,\ OH}$); 1622 m, 1584 m ($\nu_{C=N}$); 747 m ($\nu_{CS}$). UV–Vis (MeOH): $\lambda_{max}$ ($\varepsilon_M$, $M^{-1}\ cm^{-1}$) 256 (12105); 321 (5980) 430 (sh) 655 (385). Electrochemistry (acetonitrile; 0.1 M $NEt_4ClO_4$; $E_c/E_a$ (mV versus Ag/AgCl): −1210/−1096, 772.

### 2.3. Synthesis of complex [Ni(py-pts)$_2$](NO$_3$)$_2$·2CH$_3$CN (**2**-(NO$_3$)$_2$)

Pyridine-2-carboxaldehyde-phenylthiosemicarbazone (py-pts), was synthesized according to the reported procedure [19] by the reaction of phenylthiosemicarbazide and pyridine-2-carboxaldehyde in methanol. A solution of py-pts (311 mg, 1.0 mmol) in 40 mL of hot methanol was mixed with a solution of $Ni(NO_3)_2{\cdot}6H_2O$ (145 g, 0.5 mmol) in 20 mL of methanol. The solution was heated at reflux for 1 h, giving rise to a dark red solution. The resulting mixture was filtered and concentrated to about 10 mL, affording a dark red crystalline solid, which was washed with a mixture of MeOH/$Et_2O$ and dried in air. X-ray quality red block crystals were formed by slow evaporation of a solution in acetonitrile/methanol over one week. Yield 325 mg, 90%. Elem. *Anal.* Calc. for $C_{30}H_{30}N_{12}NiO_6S_2$: C, 46.35; H, 3.89; N, 21.62. Found: C, 46.22; H, 3.01; N, 21.34%. IR (KBr, $cm^{-1}$): 3416 w ($\nu_{NH}$); 1614 m ($\nu_{C=N}$); 782 m ($\nu_{CS}$); 1383 s ($\nu_{NO}$ UV–Vis (MeOH): $\lambda_{max}$ ($\varepsilon_M$, $M^{-1}\ cm^{-1}$) 250 ($2.8 \times 10^4$); 372 ($2.7 \times 10^4$); 424 (sh) 806 (72). Electrochemistry (acetonitrile; 0.1 M $NEt_4ClO_4$; $E_c/E_a$ (mV versus Ag/AgCl): 462/556.

### 2.4. X-ray crystallography

Single crystal X-ray diffraction data for complexes **1** and **2**-$(NO_3)_2$ were collected using a Bruker Kappa ApexII diffractometer. Suitable crystals were identified under a polarizing microscope, affixed with oil (Paratone-n, Exxon) in a Hampton Research Cryoloop, and transferred to the cold nitrogen stream of the diffractometer. The temperature at the crystal was maintained at 150 K using a Cryostream 700 EX low-temperature apparatus (Oxford Cryosystems). The unit cells were determined from the setting angles of the reflections collected in 36 frames of data. Data were measured using graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) collimated to a 0.6 mm diameter and a CCD detector at a distance of 50 mm from the crystal with a combination of phi and omega scans. A scan width of 0.5° and scan time of 10 s were employed. Data collection, reduction, structure solution, and refinement were performed using the Bruker Apex2 suite (v2.0-2) [20]. All available reflections to $2\theta_{max}$ = 52° were harvested and corrected for Lorentz and polarization factors with Bruker SAINT (v6.45) [21]. Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS 2004/1 [22]. The structures were solved by direct methods and refined using a full-matrix least squares-based method on $F^2$ (SHELXL-97) within the WINGX package [23]. All non-hydrogen atoms were refined using

**Table 1**
Crystal data and structure refinement for complexes **1** and **2**-$(NO_3)_2$.

| | **1** | **2**-$(NO_3)_2$ |
|---|---|---|
| Empirical formula | $C_{28}H_{22}N_6Ni_2S_4$ | $C_{30}H_{24}N_{12}NiO_6S_2$ |
| Formula weight | 688.18 | 771.42 |
| Temperature (K) | 150 | 150(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic |
| Space group | *C*2/*c* | *C*2/*c* |
| *a* (Å) | 27.562(12) | 20.568(5) |
| *b* (Å) | 7.963(4) | 12.316(5) |
| *c* (Å) | 13.303(6) | 15.551(5) |
| *β* (°) | 112.298(17) | 117.519(5) |
| *V* (Å$^3$) | 2701(2) | 3494(2) |
| *Z* | 4 | 4 |
| $D_{calc}$ (g $cm^{-3}$) | 1.692 | 1.467 |
| *μ* ($mm^{-1}$) | 1.736 | 0.736 |
| *F*(000) | 1408 | 1584 |
| Crystal size (mm) | 0.40 × 0.26 × 0.14 | 0.25 × 0.24 × 0.19 |
| *θ* Range (°) | 1.60–27.53 | 2.15–26.00 |
| Reflections collected | 33279 | 25961 |
| Independent reflections ($R_{int}$) | 4121 (0.0885) | 3436(0.1057) |
| Data/restraints/parameters | 4121/0/181 | 3436/0/231 |
| Goodness-of-fit (GOF) on $F^2$ | 1.074 | 1.042 |
| Final *R* indices [$I > 2\sigma(I)$] | *R*1 = 0.0438, *wR*2 = 0.0944 | *R*1 = 0.0528, *wR*2 = 0.1247 |
| *R* indices (all data) | *R*1 = 0.0775, *wR*2 = 0.1169 | *R*1 = 0.0844, *wR*2 = 0.1442 |
| Largest difference in peak/hole (e Å$^{-3}$) | 0.773/−0.894 | 0.536/−0.475 |