A New Mononuclear Thiolato Nickel(II) Square Planar Complex with an Uncommon (S2NO) Coordination

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Abstract

The synthesis, structure, spectra and properties of (Ph$_4$P)[Ni(MSA)(SPh)] (tetraphenylphosphonium 2-(2-mercaptophenyl)salicyladiminato thiophenolato nickelate(II)) (I) are reported. The compound crystallizes as red needles in the monoclinic spaces group $P2_1/c$ with cell dimensions $a = 10.813(6)$, $b = 17.061$-(6), $c = 19.873(10)$ Å, $\beta = 100.06(5)°$, $V = 3610(3)$ Å^3, $Z = 4$. The structure was solved by conventional methods using 4919 reflections and refined to $R = 5.7\%$ and $R_w = 6.6\%$. The complex features a square planar Ni^{2+} environment in which the metal center is bound to two sulfur, a nitrogen an an oxygen atom. The corresponding phenolato complex (Ph$_4$P)[Ni-(MSA)(OPh)] (II) is X-ray isomorphous to I. The electronic spectra and electrochemical properties of I and II are discussed.

The importance of Ni in biology has been increasingly recognized in recent years [1]. Ni resides at the active sites of several classes of important metalloenzymes such as ureases [2a], methylcoenzyme reductases [2b], hydrogenases [3] and CO dehydrogenases [4] from a variety of organisms. Ni EXAFS studies on several hydrogenases [5] indicate a mononuclear Ni center surrounded by sulfur ligands (probably cysteinyl) with the presence of nitrogen or oxygen ligands being uncertain, but not ruled out. An important feature of the Ni centers in these enzymes is their ability to shuttle between 2+ and 3+ states. To date, an accurate synthetic model for the Ni active site in any of the above enzymes is not available, although several Ni(SR)$_4^{2-}$ [6, 7] and NiN$_m$(SR)$_n$ [8] complexes exist. It should also be noted that the structural details of the Ni active sites differ from enzyme to enzyme [1]. Although a large number of Ni complexes exist, none of them was prepared from a perspective outlined above.

Recently, Kruger and Holm [9] demonstrated the accessibility of Ni^{3+} sites in the presence of thiolato moieties of the Ni[*N,N'*-ethylenebis(*o*-mercaptobenzamide)]$^{2-}$ complex. In this respect, the work of Sugiura *et al.* [10] on SH containing peptide/Ni^{3+} complexes in frozen solutions is also noteworthy.

Here we wish to report the properties of a structurally relevant, new mononuclear Ni^{2+} complex with an uncommon NiONS$_2$ coordination containing thiolate sulfur. During the preparation of this report, two related complexes based on the pyridine-2,6-dimethanethiolate (pdmt) ligand, [Ni(pdmt)(SR)]$^-$ (R = Et, Ph) have been published [11].

Treatment of bis[2-(2-mercaptophenyl)salicyladiminatodinickel(II,II) [12] (abbr. [Ni(MSA)]$_2$) with 2 eq. of KSPh under inert atmosphere, in minimum volume CH$_3$CN followed by the addition of 2 eq. Ph$_4$PCl and subsequent removal of KCl by filtration, afforded diamagnetic red needles [13] of [Ph$_4$P][Ni(MSA)(SPh)] (I) in 89% yield. The use of NaOPh afforded the X-ray isomorphous orange–red [Ph$_4$P][Ni(MSA)(OPh)] (II)* in 76% yield. Though not as critical in the synthesis of I, dry CH$_3$CN must be used in II to ensure product crystallization.

Acetonitrile solutions of I are air-sensitive. The decomposition products are [Ni(MSA)]$_2$ and (PhS)$_2$ as determined by ^{1}H NMR and mass spectroscopy. The electronic spectra of I and [Ni(MSA)]$_2$ are shown in Fig. 1. In I, absorptions occur at 491 ($\epsilon = 5568$ M^{-1} cm^{-1}), 413 (7055) and 300(sh) (26 360) nm. The low energy absorption is highly dependent on the donor ability of the monodentate ligand and is assigned to a charge-transfer transition from this ligand to the metal. Thus, when PhS$^-$ is replaced by PhO$^-$ and *o*-aminothiophenolate, the low energy absorption shifts to 450 and 502 nm, respectively as expected. No significant shift of the 413 nm band is observed which is due to transitions within the tridentate MSA ligand.
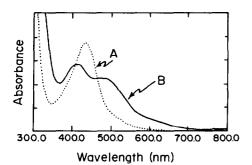

Fig. 1. Optical spectra of dimethylformamide solutions of (A) [Ni(MSA)]$_2$ and (B) [Ni(MSA)(SPh)]$^-$. It should be noted that in DMF [Ni(MSA)]$_2$ is dissociated to the monomeric Ni(MSA)(DMF).
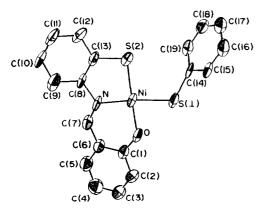

Fig. 2. ORTEP representation (50% probability ellipsoids) and labeling scheme of [Ni(MSA)(SPh)]$^-$. S(1)–Ni–S(2), 95.33(4)°; S(1)–Ni–O, 81.92(7)°; S(1)–Ni–N, 174.52(9)°; S(2)–Ni–O, 176.45(8)°; S(2)–Ni–N, 90.07(9)°; O–Ni–N, 92.7(11)°; Ni–S(1)–C(14), 119.83(11)°; Ni–S(2)–C(13), 97.26(12)°; Ni–O–C(1), 129.09(21)°.

In the solid state, see Fig. 2, the Ni center is found in a square planar environment with two cis-sulfur atoms of the MSA$^-$ and PhS$^-$ ligands at 2.144(1) and 2.212(1) Å, respectively. These are shorter than those found in the tetrahedral Ni(SPh)$_4$$^{2-}$ [6b] (2.292(5) Å) and comparable to those in [Ni(pdmt)-(SPh)]$^-$ at 2.169(2) and 2.173(2) Å respectively. In the latter complex, the Ni center also adopts a square planar geometry. Similar Ni–S distances are also found in the trinuclear [Ni$_3${SCH(CH$_3$)-COO}$_4$]$^{2-}$ [13] and [Ni(S$_2$C$_2$(CN)$_2$)$_2$]$^{2-}$ [14] at 2.182(2) and 2.165(9) Å respectively. The Ni–O and Ni–N distances at 1.865(2) and 1.917(2) Å, respectively are within the range found in bis(alkyl-salicyldeneiminato)Ni complexes [15]. A more detailed description of the crystal structure will be reported later.

EXAFS studies of the Ni center in carbon monoxide dehydrogenase from *Clostridium thermo-aceticum* by Cramer *et al.* [5d] show that the best fit to the experimental data is obtained in a model with two Ni–S bonds at 2.21 Å and approximately two Ni(N,O) bonds at 1.97 Å. I is unique in this respect because it is the first structurally characterized mononuclear Ni complex with a mixed S2NO coordination and displaying Ni-Ligand distances which are in excellent agreement with the aforementioned EXAFS results.

Cyclic voltammetric results in CH$_3$CN (using a Pt working electrode and 0.1 M Bu$_4$NClO$_4$ as supporting electrolyte; SCE = saturated calomel electrode) show that I is incapable of supporting a Ni^{3+} state, oxidizing irreversibly at 0.253 V (versus SCE) to yield [Ni(MSA)]$_2$ [12] and (PhS)$_2$. This is not surprising due to the ease of oxidation of the terminal PhS$^-$ ligand and is in accord with the electrochemical behavior of other Ni–SR complexes (i.e. Ni(SPh)$_4$$^{2-}$ [6a, 7a] [Ni$_4$(SEt)$_{12}$]$^{2-}$ [7a].

(Ph$_4$P)[Ni(MSA)(SPh)] appears to be an interesting structural model particularly for CO dehydrogenase from *Clostridium thermoaceticum*. Although the type of tridentate ligand (MSA) used here is not likely to stabilize a Ni^{3+} center* at a potential similar to that found in the enzymes (−150 to −400 mV), it is still attractive for it allows for the systematic variation of the coordination sphere of Ni from (ONS) to (SNO), (SNS), and (ONO) through appropriate modification in the MSA ligand [17]. Further variation in the coordination sphere of Ni can be achieved by changing the terminal –SPh group by other anionic sulfur oxygen or nitrogen donor ligands [17]. This electronic and isostructural series of mononuclear Ni complexes (the first member of which is reported herein) with systematically controlled ligation of sulfur, oxygen and nitrogen should serve as a good source of model compounds for future EXAFS, XANES studies. However, the inability to access a stable Ni^{3+} state precludes consideration of I as an accurate functional model. The factors stabilizing a Ni^{3+} state in the presence of anionic sulfur ligands and other biologically relevant moieties are under investigation.

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*Electrochemical studies of the [Ni(MSA)]$_2$ complex in DMF, acetonitrile, CH$_2$Cl$_2$ and DMSO indicate that Ni^{3+} cannot be stabilized. Instead, ligand oxidation occurs to form a dimer containing disulfide bonds [16].

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