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NICKEL THIOLATES. SIMPLE SYNTHESIS, THE BEHAVIOR UPON PROTOLYSIS AND OXIDATION POTENTIALS

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$(NEt_4)_2[Ni(SPh)_4]$, $(NEt_4)_3[Ni_3(SEt)_{12}]$ and $(NEt_4)_2[Ni_2(edt)_3]$, (edt=ethan-1,2-dithiolate dianion), were synthesized by a simple method. These complexes were condensated stepwise by controlled protolysis through their own higher clusters such as $[Ni(SEt)_2]_n$ ($n \neq \infty$) and $(NEt_4)_2[Ni_3(edt)_4]$ to the polymers, $[Ni(SPh)_2]_\infty$, $[Ni(SEt)_2]_\infty$, and $[Ni(edt)]_\infty$.

Metal-simple thiolate systems[1-8] arouse our concern as those relate to two different regions, bioinorganic chemistry and structural chemistry due to their structural diversity.[4] The recent study on the nickel sites of so called "uptake" hydrogenases[9] has revealed that they are high valent nickel(III), and placed in a low spin (S=1/2) anisotropic ligand field showing almost superimposable EPR signals to each other,[9,10] and that the nickel is surrounded by the three sulfur atoms as the dominant EXAFS scatterers.[11] Unfortunately, the chemistry of nickel thiolates has not been developped well, because this combination has been known unfruitful as trends to give insoluble polymers,[2b] except a few cases, $(PPh_4)_2[Ni(SPh)_4]$,[2a] $[Ni(SEt)_2]_6$[2b] and $(NEt_4)_2[Ni_2(S_2\text{-}o\text{-}xyl)_3]$, ($S_2$-o-xyl=o-xyl-α,α'-dithiolate),[2c] where the soluble or the crystallizable compounds were isolated accidentally or obtained through multi-step synthesis. We wish to report in this letter a simple preparative method of nickel-simple thiolates, the condensation feature of the compounds upon protolysis, and the data of cyclic voltammetry.

An example of the new synthesis is given below for the compound $(NEt_4)_2$-$[Ni(SPh)_4]$ (1). $(NEt_4)_3[Ni_4(SEt)_{12}]$ (2) and $(NEt_4)_2[Ni_2(edt)_3]$ (3) were synthesized by the similar way under anaerobic conditions in dried media.[12,13] $(NEt_4)_2[Ni(SPh)_4]$: A solution of 15 mmol of $(NEt_4)_2[NiBr_4]$ in 120 cm^3 of dried acetonitrile was added dropwise to a stirred suspension of 60 mmol of NaSPh in 100 cm^3 of dried acetonitrile at ambient temperature under an anaerobic condition. After 5 h of stirring, the resulting NaBr and insoluble materials were removed from the mixture by filtration. The red brown filtrate was concentrated to ca. 50 cm^3 and placed in a refrigerator (-10 °C). The crude crystals appeared in the solution were collected, and recrystallized from acetonitrile again. Yield 6.5 g (57%).[14]

The structure of the anionic part of this compound is shown in Fig. 1 with its molecular geometry.[15]

In metal thiolate systems of manganese,[4] iron,[5] cobalt,[3] and copper,[1] the appaerance of the structural variations depends on the initial molar ratios of the reactants, RS^-/M. However, in nickel thiolates, the continuous diminish of RS^-/Ni ratio from 4 to 2 did not seem to lead to the formation of higher order clusters such as $[Ni_4(SPh)_{10}]^{2-}$, the homologue of $[M_4(SPh)_{10}]^{2-}$; M=Mn,[4b] Fe,[5a] Co,[3c] which shows the adamantanelike skeleton. As the ratio RS^-/Ni was decreased from 4 to 2, the amount of the compounds 1 - 3 decreased and the yield of the polymers $[Ni(SR)_2]_\infty$ increased.

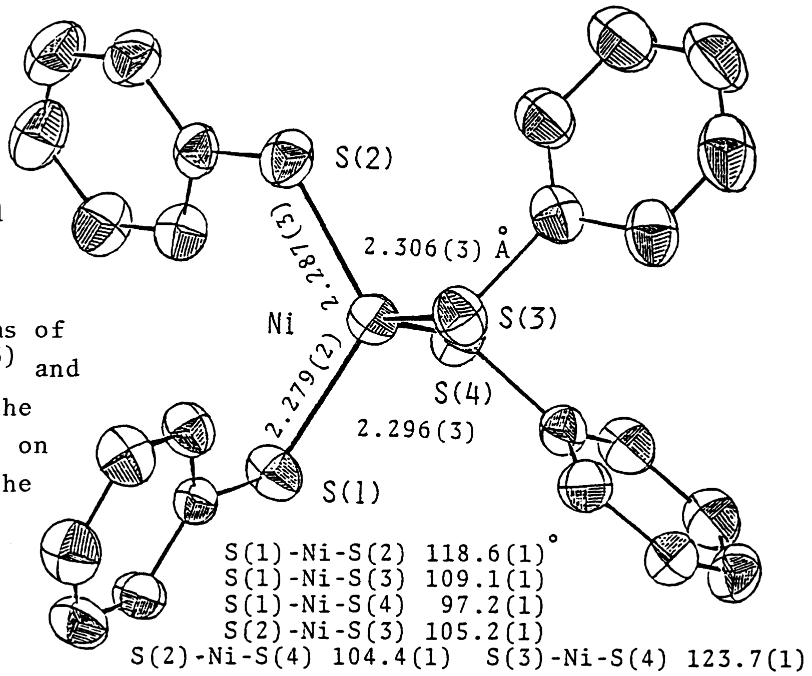
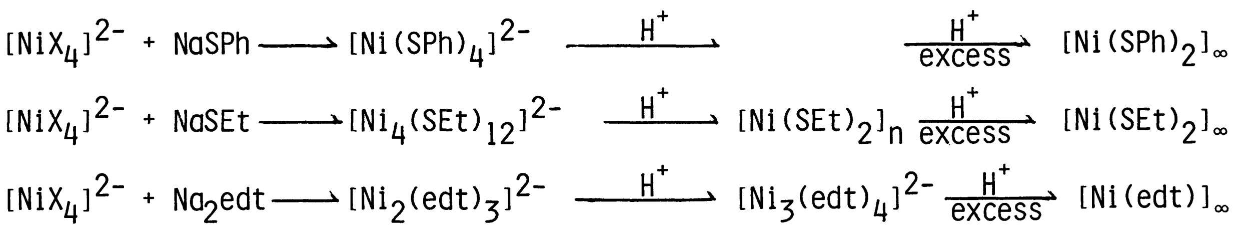


Fig. 1. The Structure of $[Ni(SPh)_4]^{2-}$.

The condensation of the nickel thiolates 1 - 3 to their own higher order clustera was achieved by operating H^+ to the solutions. The acetonitrile solution of 2 Or 3 precipitated in good yield the crystals of $[Ni(SEt)_2]_n$ ($n \neq \infty$) (4)[16] or $[Ni_3(edt)_4]^{2-}$ (5)[17] as analyzed, when treated with small amount of H_2O almost equimolar to the solute, or treated with $CHCl_3$ involving 1% of EtOH. The excess amount of H_2O or EtOH separated the polymers $[Ni(SPh)_2]_\infty$, $[Ni(SEt)_2]_\infty$ and $[Ni(edt)]_\infty$ from the solutions. The result is summarized in Scheme 1. From this, we perceive that the key point in the expansion of nickel thiolate chemistry lies in the control of H^+ amount. The condensation pattern upon protolysis varies with thiolate ligand according to the structure and the electronic property of the thiolate.



Scheme 1.

The electrochemical processes of these compounds were all irreversible. The anodic oxidation feature of their cyclic voltammetry was complicated, suggesting the sequencial decomposition of the oxidized species on the electrode. The list of the initial anodic peak potentials is shown in Table. 1.

The high oxidation state of nickel in the hydrogenases is easily achieved under air. In fact, the redox potentials of the enzymes distribute in -150 mV – -220 mV (vs. NHE).[18] This is far lower than the usual Ni(III)/Ni(II) redox potentials as pointed out before.[10] Thiolate or sulfide ligands are, however, known to stabilize high oxidation state of metals.[4] For instance, in nickel itself, NiS is easily oxidized to NiS(OH) in moistened air.[19] The result in Table 1 exhibits that the nickel thiolates with $RS^-/Ni \geq 3$ have in practice low oxidation potentials close to those of nickel containing hydrogenases. However, considering the differences in the conditions of electrochemistry between our cases and hydrogenases, the potentials of the obtained compounds are not enough. Low oxidation potentials comparative to those of hydrogenases will be achieved in nickel tetraalkylthiolates of EtS^-, Bu^tS^-, edt^{2-}, and so on.

Table 1. Anodic Peak Potentials (vs. SCE, in DMSO, 0.1 M TEAP, glassy carbon electrode)

Ni Thiolate	E_{pa}/V
$[Ni(SPh)_4]^{2-}$	-0.12
$[Ni_2(edt)_3]^{2-}$	-0.23
$[Ni_3(edt)_4]^{2-}$	1.46
$[Ni_4(SEt)_{12}]^{2-}$	-0.13
$[Ni(SEt)_2]_n$ (n≠∞)	0.04

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12) $(NEt_4)_2[Ni_4(SEt)_{12}]$; From the reaction mixture of $(NEt_4)_2[NiCl_4]$ (15 mmol) and NaSEt (60 mmol) in acetonitrile, the insoluble materials were removed. The solvent was replaced to a 180 cm^3 of acetone. This immediately precipitated brown black crystals. They were collected by filtration, washed, and again recrystallized from acetone at - 10 °C. Air sensitive greenish brown mica. Yield 4.8 g (72% to the Ni). Found: C,41.17; H,8.71; N,3.23; Ni,17.79%. Calcd for $C_{48}H_{120}N_3Ni_4S_{12}$: C,41.38; H,9.06; N,3.15; Ni,17.59%. UV-VIS (acetonitrile): 318 nm (ε=37900), 410 (sh 14600).

13) $(NEt_4)_2[Ni_2(edt)_3]$; Removal of NaBr, insoluble materials and the solvent from the reaction mixture including 15 mmol of $(NEt_4)_2[NiBr_4]$ and 60 mmol of Na_2edt in acetonitrile afforded a black residue, which was washed well with acetone and dissolved into acetonitrile again. After filtering off the black crystals of $(NEt_4)_2[Ni_3(edt)_4]$, the green crystals of the $[Ni_2(edt)_3]^{2-}$ salt were grown up slowly in the concentrated solution (20 cm^3) at - 10 °C. Yield 2.7 g (55% to the Ni). Found: C,40.05; H,8.79; N,4.22; Ni,17.73%. Calcd for $C_{22}H_{52}N_2Ni_2S_6$: C,40.38; H,8.01; N,4.28; Ni,17.94%. UV-VIS (acetonitrile): 468 nm (ε=2990), 620 (718). Air sensitive.

14) Found: C,63.58; H,8.86; N,3.80; Ni,7.58%. Calcd for $C_{40}H_{60}N_2NiS_4$: C,63.56; H,8.00; N,3.70; Ni,7.77%. UV-VIS (acetonitrile): 302 nm (ε=37100), 430 (sh 6000), 660 (sh 780), 1750 (58). Air sensitive as reported.[2a)]

15) The NiS_4 structure of this compound is the same as that of the PPh_4 salt.[2a)] Whereas a difference in the orientation of C_6H_5(S) rings. Crystal data: F.W.= 755.874, Monoclinic, space group $P2_1/a$, a=14.842(3), b=22.706(6), c=12.058(2) Å, β=93.58(2)°, V=4054(2) $Å^3$, Z=4, Dx=1.238 g cm^{-3}, μ(Cu Kα)=2.78 mm^{-1}, R=8.8% for 5154 reflections. A positional disorder at the α carbons in one of NEt_4^+.

16) $[Ni(SEt)_2]_n$ ($n \neq \infty$); Found: C,26.65; H,5.47; N,0%. Calcd for $C_4H_{10}NiS_2$: C,26.55; H,5.57; N,0%. Fairly stable in air. This compound is soluble in DMSO or DMF, hence, will not be assigned to the polymer but to the hexamer $[Ni(SEt)_2]_6$.[2b)]

17) $(NEt_4)_2[Ni_3(edt)_4]$; Found: C,35.43; H,6.81; N,3.59; Ni,21.87%. Calcd for $C_{24}H_{56}N_2Ni_3S_8$: C,35.79; H,7.01; N,3.48; Ni,21.87%. UV-VIS (acetonitrile): 392 nm (ε=2200), 468 (1280). Comparatively stable in air.

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