New Synthesis, Properties, and the Formation of the Hexamer of Nickel(II) Ethanethiolate, $[Ni(SEt)_2]_6$

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$[Ni_3(SEt)_8]^{2-}$ reacted with water in acetone to give the known hexameric ring compound, $[Ni(SEt)_2]_6$, where SEt means $CH_3CH_2S^-$. The $[Ni(SEt)_2]_6$ was oxidized electrochemically in a quasi-reversible manner at +0.60 V (vs. SCE) in CH_2Cl_2. ^1H and ^{13}C NMR revealed that this compound has two types of -SEt (low- and high- field types; the chemical shift discrepancy is ca. 0.4 ppm for ^1H NMR), probably corresponding to the axial-equatorial configurations of the thiolate. The formation of the cyclic hexamer in CH_3CN and $CHCl_3$ in the presence of protic reagents was studied.

Metal complexes of simple thiolates (alkanethiolates or arenethiolates) are now substances that are of topochemical interest as potential sources of a variety of multi-nuclear compounds because of the bridging disposition of thiolate ligands.[1] The hexagonal molecular cycles, $[Ni(SEt)_2]_6$,[2] (Fig. 1),[3] $[Ni(SCH_2CH_2OH)_2]_6$,[4] $[Pd(SCH_2CH_2OH)_2]_6$,[5] the tetragonal analogue, tetrakis[bis-(*N*-methylpiperidine-4-thiolato) nickel],[6] and the octagonal analogue, $[Ni(SCH_2CH_2COOEt)_2]_8$,[7] form a novel topochemical group by their ring crown structure, with linked square planar units of M(II) (M=Ni and Pd) and bridging thiolates. The M-S frameworks of these compounds hold inside cylindrical vacancies surrounded by arrays of coplanar metal centers. This salient structural feature, the so called "tiara",[2] involves the possibility of developing new types of inclusion complexes. In practice, $[Ni(SCH_2CH_2COOEt)_2]_8$ takes one of the substituent pendant groups (-OEt) in a solid into its own hole by anchoring the ester oxygen to nickel atoms.[7]

In spite of its central situation in the tiara group, almost no efforts have been made to elucidate its basic character of the hexamer, $[Ni(SEt)_2]_6$, since the detouring[2a,c] synthesis and a structural short communication.[2b] In the course of our study of nickel-thiolate systems,[8] we have found a simple way to obtain the hexamer. This paper will present a description of the new synthetic method, aspects of the formation in aprotic media, and the result of the usual physicochemical measurements (NMR and electrochemistry).

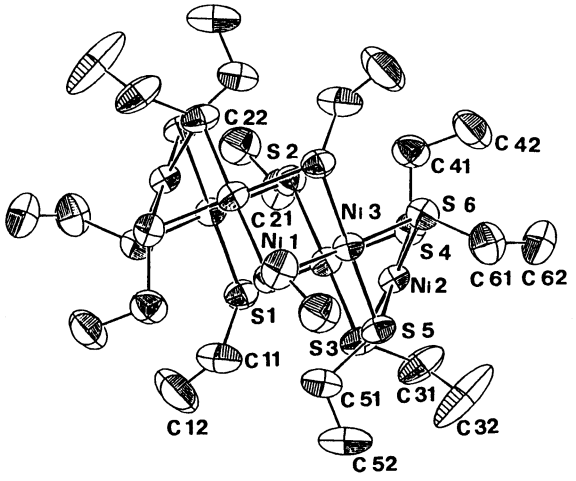

Fig. 1. ORTEP plot of the non-hydrogen atoms of $[Ni(SEt)_2]_6$ (triclinic) with 50% probability thermal elipsoids and the atom numberlings.[3]

Experimental

Every synthetic procedure was performed under a nitrogen or argon atmosphere. The solvents were refluxed over appropriate drying agents and distilled under argon. Sodium ethanethiolate was prepared from sodium and excess ethanethiol in methanol and dried completely (120 °C, in vacuo) before use.

Preparation of the Materials. $(NEt_4)_2[Ni_3(SEt)_8]$ was prepared according to A. D. Watson's method.[9]

$[Ni(SEt)_2]_6$: To a greenish brown solution of 0.50 g (0.37 mmol) of $(NEt_4)_2[Ni_3(SEt)_8]$ in 450 ml of acetone was added 0.2 g of commercial $[NMe_3Ph]^+Cl^- \cdot nH_2O$ (in acetone). The solution was then refluxed for 30 min, cooled to room temperature, and passed through a sintered glass to remove any insoluble impurities (red brown powder and an extra amount of $[NMe_3Ph]^+Cl^- \cdot nH_2O$). The filtrate, wine red in color, was placed in a refrigerator at −20 °C for 2 weeks. The black crystals which slowly grew in the flask were collected and dried in vacuo. Stable in air. Yield, 0.21 g (72%). Found: C, 26.65; H, 5.45; N, 0%. Calcd for $C_{24}H_{60}Ni_6S_{12}$: C, 26.55; H, 5.57; N, 0%. Absorption spectrum (in chloroform): 335 nm (ε=55600), 407 (20100), 515 (7030), 570 (sh, 5430). Soluble in benzene, toluene, xylene, chloroform, and dichloromethane. Slightly soluble in ethyl acetate. Insoluble in acetone, acetonitrile, dimethyl sulfoxide, ethanol, and water.

Physicochemical Measurements. The electronic spectra were recorded on a Hitachi Recording Spectrometer 340. The ^1H NMR spectra were obtained by the use of JEOL FX-90Q spectrometer. Electrochemical measurements were carried out by using a Yanaco Polarographic Analyzer, model P-1100, or a Hokuto Potentiostat/Galvanostat HA-201 in connection with a Fuso function generator, model 321. the molecular weight of the hexamer in solution was decided by the use of a Knauer Vapor Pressure Osmometer No. 01.00.

Results

The molecular weight of the "tiara" in benzene was

decided as 1100 (accuracy 10%) by means of vapor pressure osmometry with benzyl (molecular weight=210.3) as the standard. This result agrees with the theoretical value for $[Ni(SEt)_2]_6$, 1080. Therefore, the hexameric aggregation is maintained also in solution, at least in benzene.

Figure 2-a depicts the absorption spectrum of $[Ni(SEt)_2]_6$ in chloroform. This is composed of an intense LMCT band at 335 nm (ε=9270 $M^{-1}cm^{-1}$/Ni (1 M=1 mol dm^{-3})) and much weaker ones at 407 nm (ε=3350 $M^{-1}cm^{-1}$/Ni), 515 nm (ε=1170 $M^{-1}cm^{-1}$/Ni, deconvoluted), and 570 nm (ε=905 $M^{-1}cm^{-1}$/Ni, deconvoluted). No absorption was observed in NIR region. The spectrum differs in its intensity from that of $[Ni_3(SEt)_8]^{2-}$ [3d] (Fig. 2-b) at ca. 400 nm and in the 500—600 nm region.[10] According to Maki,[11] the bands at 407, 515, and 600 nm of the hexamer are to be assigned to the d-d transitions, $^1A_{1g}\rightarrow{}^1A_{2g}$, $^1B_{2g}$, and $^1A_{1g}\rightarrow{}^1E_g$ respectively, of a square planar Ni(II), judging from their wavelength regions and intensities.[12]

The ^1H NMR spectrum of the hexamer (in chloroform, at room temperature) is shown in Fig. 3-a. The spectrum reveals that two types of ethanethiolate, different in the strength of their diamagnetic shielding, exist in the solution. The correlation between the methylene and methyl protons of each EtS^- was decided by means of proton-proton decoupling technique (depicted in the figure). The observed chemical shifts of the methyl and methylene protons of the high-magnetic-field -SEt (CH_2; δ=1.76, CH_3; δ=1.08) agree well with those of $[Ni_2(SEt)_6]^{2-}$ (CH_2; δ=1.79—1.87, CH_3; δ=1.05 and 1.20) and $[Ni_3(SEt)_8]^{2-}$ (CH_2; δ=1.85—1.88, CH_3; δ=1.04—1.08).[13] Compared with these, the values of the low-magnetic-field -SEt are shifted ca. 0.4 ppm downward. The result of ^{13}C NMR indicates the same situation, showing that 4 kinds of carbon atoms exist in the solution (Fig. 3-b). The peaks were assigned by means of selective decoupling technique. (Low field -SEt: CH_2; δ=26.367, CH_3; δ=19.446. High field -SEt: CH_2; δ=20.177, CH_3; δ=16.229.)

The electrochemical behavior of $[Ni(SEt)_2]_6$ in dichloromethane (0.2 M $NBu^n_4PF_6$, vs. SCE, glassy carbon electrode) was studied over the potential range from −1.8 to +1.8 V by means of cyclic voltammetry (CV) at various scan rates (10—200 mV s^{-1}) and by means of differential pulse polarography (DPP) with a modulation amplitude 10 mV. No evidence for the reduction of the hexamer corresponding to the formation of the monoanion $[Ni(SEt)_2]_6^-$ was obtained in the region observed. The CV chart exhibited three oxidation peaks at +0.655, +1.05, and +1.61 V, within which the higher two were irreversible. Cyclic scans limited within 0.8 to 0 V revealed that the +0.655 V anodic peak was followed by a cathodic peak at +0.55 V (see Fig. 4). No scan rate dependence was observed for either anodic or cathodic peaks. That is, we obtained the relationship $(\partial E/\partial \log v)_T=0$,[17] which is applicable to reversible and quasireversible cases, while the cathodic anodic current ratio, i_{pc}/i_{pa},[18] calculated for the case of a 100 mV s^{-1} scan rate, was 0.92. Consequently, the oxidation process was quasireversible. This was also confirmed by DPP measurements. The

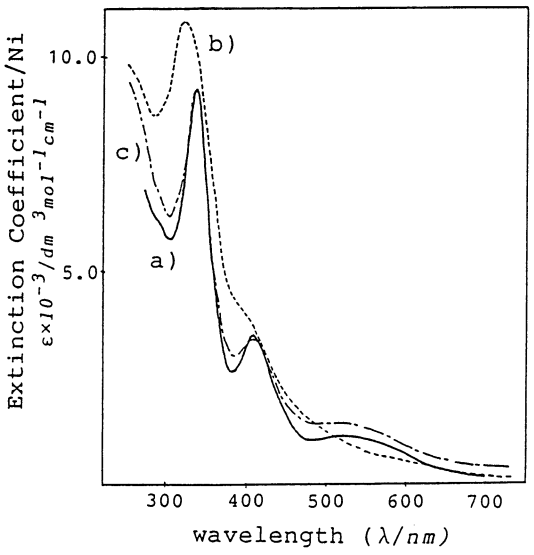

Fig. 2. Absorption spectra converted for extinction coeffient/Ni. a) $[Ni(SEt)_2]_6$ in $CHCl_3$ (commercial), b) $[Ni_3(SEt)_8]^{2-}$ in CH_3CN (dried over CaH_2), c) $[Ni_3(SEt)_8]^{2-}$ in $CHCl_3$ (commercial) or in CH_3CN (dried over CaH_2) with exess amount of $NEt_3H\cdot BF_4$.

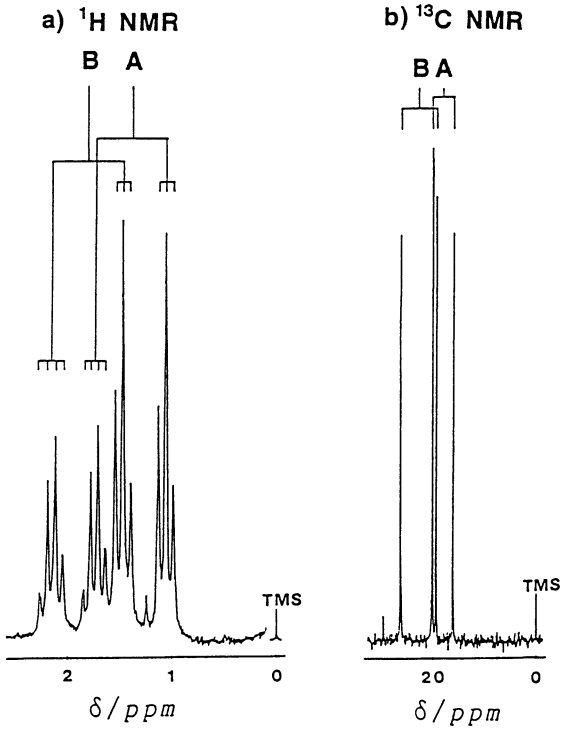

Fig. 3. NMR spectra of $[Ni(SEt)_2]_6$ in $CDCl_3$: a) ^1H NMR; A; high field EtS^-, B; low field EtS^-. b) ^{13}C NMR; A; high field EtS^-, B; low field EtS^-. TMS internal standard.

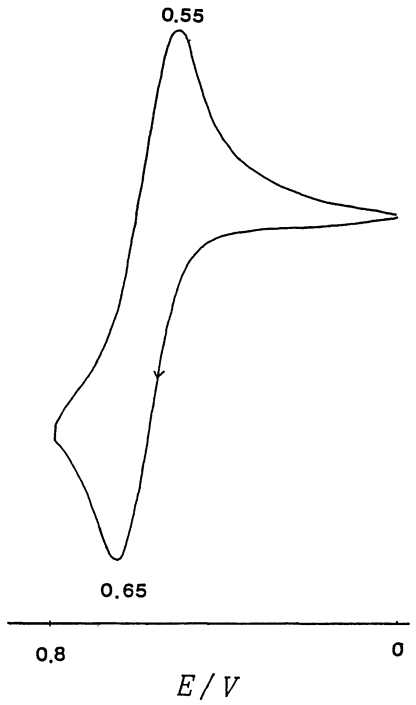

Fig. 4. The cyclic voltammogram of $[Ni(SEt)_2]_6$ in CH_2Cl_2 (scan range +0.8—0 V, vs. SCE, 0.2 M $NBu^n_4PF_6$, glassy carbon electrode).

half height width, 100 mV, was slightly larger than the ideal reversible case (91 mV).[19]

The effects of ethanol, water, and H^+ itself on the hexamer generation were also examined. The absorption spectra of (a) $[Ni(SEt)_2]_6$ in $CHCl_3$ (b) $[Ni_3(SEt)_8]^{2-}$ in CH_3CN, and (c) $[Ni_3(SEt)_8]^-$ in commercial $CHCl_3$ including 1% EtOH are depicted in Fig. 2, with the extinction coefficient *per* Ni on the ordinate. As may be seen in Fig. 2, the major species in the $[Ni_3(SEt)_8]^{2-}/CHCl_3$ (commercial) solution was not $[Ni_3(SEt)_8]^{2-}$ itself, but $[Ni(SEt)_2]_6$, while the amount of the hexamer generated in commercial $CHCl_3$ was the same as in (b). Consequently, almost all of the $[Ni_3(SEt)_8]^{2-}$ was converted to the hexamer in commercial $CHCl_3$. On the other hand, in a purified $CHCl_3$ (dried with H_2SO_4, hence including almost no alcohol for stabilization) the original absorption spectrum of $[Ni_3(SEt)_8]^{2-}$, which was observed in dried acetonitrile, changed in a different way. In this case the spectrum changed inconspicuously in the 500—600 nm region both in spectral shift and in intensity. On the other hand, in the 300—400 nm region, the original peaks at 316 nm and 400 nm (sh) shifted to 330 nm and 416 nm respectively. Especially the latter peak grew remarkably. The reaction which accompanied this incomplete absorption change was also studied by ^1H NMR in dried $CDCl_3$. However, the results were not unequivocal except that the signals characteristic of the hexamer appeared only slightly. This means that the significant step generating the hexamer proceeds in the presence of EtOH. The addition of EtOH afforded the hexamer's spectrum also in acetonitrile. $[Ni(SEt)_2]_6$ was also generated in acetone by the addition of an almost equimolar amount of water to the trimer, as has been described above in discussing the synthesis.

The effect of water was more rigorous, and the use of excess water yielded an insoluble polymer, $[Ni(SEt)_2]_\infty$, in acetone or acetonitrile. For example, when 0.454 mM of $[Ni_3(SEt)_8]^{2-}$ in acetonitrile (dried 3 days over CaH_2; 1g/200 ml) was treated with water (5.0 equiv), the absorption pattern changed to one which resembled the hexamer's, but more gentle, and the intensity diminished to ca. 1/2 of the theoretical value within 4 h. However, 25 equiv of water led to a pseudo-exponential decomposition of $[Ni_3(SEt)_8]^{2-}$ with a decay constant of $k=1.29\times10^{-4}$ s^{-1} and yielded insoluble polymers. Eventually, the formation reaction of the hexamer from $[Ni_3(SEt)_8]^{2-}$ and water competed with polymerization processes. These results led us to the idea that the H^+ originating from EtOH or water play an important role in the hexamer formation or at least in the elongation of an open chain $[Ni(SEt)_2]_n(SEt)_2^{2-}$. The effect of H^+ was examined in a more direct manner by using $[NHEt_3]^+[BF_4]^-$ to $[Ni_3(SEt)_8]^{2-}$ in acetonitrile. The result was satisfactory. Immediately after mixing, the absorption spectrum changed from that of $[Ni_3(SEt)_8]^{2-}$ to one similar to the hexamer's spectrum, just as is observed in the $[Ni_3(SEt)_8]^{2-}/CHCl_3$(commercial) system.

Consequently, the reaction described as Eq. 1 proceeds in commercial $CHCl_3$, wet acetonitrile, or wet acetone:

$$2(NEt_4)_2[Ni_3(SEt)_8] \xrightarrow{(H^+)} [Ni(SEt)_2]_6 + 4(NEt_4)(EtS) \quad (1)$$

It should be added that the isolation of the crystalline hexamer from a chloroform solution was impossible, probably due to contamination by other oligomeric species.

Discussion

The synthesis of $[Ni(SEt)_2]_6$ was first achieved by the reaction of bis(alkylthio)dialkyltin with nickel chloride in cold ethanol.[2a] The hexamer was also synthesized from tetracarbonylnickel and dialkyldisulfides in benzene by the same authors.[2c] A simple synthesis of this compound from commercial nickel salts and ethanethiol in protic media has not yet been published. The condition of such synthesis in aprotic media (chloroform, acetonitrile) is, as has been studied in this work, not straightforward; it is suggestive of the necessity of mild protic conditions. The mixing of an excess amount of water promotes the formation of uncharacterizable polymer. However, as for the other thiols, the aspect is not so tedious. In practice, $[Ni(SCH_2CH_2OH)_2]_6$, and $[Ni(SCH_2CH_2COOEt)_2]_8$, are readily prepared from simple nickel salts and the corresponding thiols in an alkaline aqueous solution[4]

and 1-propanol[7] respectively. Dance and his coworkers referred briefly to an aqueous system in relation to the chain elongation of multinuclear Ni-SR.[7] According to them, in $Ni^{2+}/^{-}SCH(CH_3)CH_2OH$ in water, $[Ni(SR)_2]_6$ predominates at 25 °C, but a series of open chain complexes, $Ni[Ni(SR)_2]_n$ ($n<30$), appear at 75 °C in an appropriate pH region. This is a result which somewhat agrees with those of our study, suggesting the participation of H^+ in chain elongation. The cyclization process might be promoted by the presence of an oxygen atom. The structure of the upper tiara, $[Ni(SCH_2CH_2COOEt)_2]_8$, in the solid state would remain the actual field where the tiara is cyclized from its open-chain precursor by anchoring to an oxygen atom and is then stabilized.

To account for the appearance of geminal EtS- signals in ^1H and ^{13}C NMR experiments, two mechanisms can be proposed: 1) the ring-current mechanism and 2) the $d\pi(Ni)$-$d\pi(S)$ interaction mechanism. The most important orbitals in the ring-current mechanism are those composed of d_z2 orbitals on Ni atoms. If we assume ca. 2 Å as the radius and six electrons for this ring orbital, the shifts calculated for the equatorial and axial methylene protons are −0.27 and +0.26 ppm respectively at the position of the methylene protons.[20] This result agrees well with the experimental result obtained by ^1H NMR, but not with the ^{13}C measurement, which afforded about 10 times as large. Consequently, it is necessary to assume for any of axial or equatorial EtS^- a $d\pi(Ni)$-$d\pi(S)$ overlap, which promotes the magnetic shielding at the ethyl groups. However, it is impossible to decide which is the low field case, axial or equatorial.

The "tiara" structure is attractive from the point of view of developing a new type of inclusion catalyst. The quasireversible oxidation of the hexamer suggests the potentiality of "tiara" compounds for inclusive oxidation catalysts.

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10) The electronic structure of $[Ni_3(SEt)_8]^{2-}$ is presumed to be complicated, reflecting its unusual structure,[9] which contains one square planar unit (central $Ni(S_b)_4$ moiety) and two strongly distorted end units ($Ni(S_b)_2(S_t)_2$). The reported dihedral angle between $Ni(S_b)_2$ and $Ni(S_t)_2$ planes is 53°.

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12) Thiolate anions are intrinsically weak ligands ranked between chloride and azide, with an usual nephelausetic effect as is manifested for the Co^{2+} and Fe^{2+} complexes.[13,14] This fact, however, does not lead to the expectation that the local geometry of $Ni(SR)_4$ is limited to Td, because LMCT is also dominant in stabilizing the "tiara" framework as well as the ligand-field stabilization. The A_{2u} array of the Ni($3d_{xz}$, $3d_{yz}$)-S(2p) orbitals in the D_{3d} symmetry is the most plausible for such stabilization. Thus, the d-d transitions of $[Ni(SEt)_2]_6$ may be said to be characterized by a square planar local symmetry perturbed with the exchange interaction due to the thiolato bridging. At any rate, an assignment based on a simple crystal field calculation is not neccesarily reliable in a square planar case because it fails to estimate the π-bonding effect.[16]

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