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Synthesis and the Structure of a Thiolato Amine Nickel Complex. (N,N'-Ethylenebis(*o*-mercaptobenzylaminato))nickel(II)

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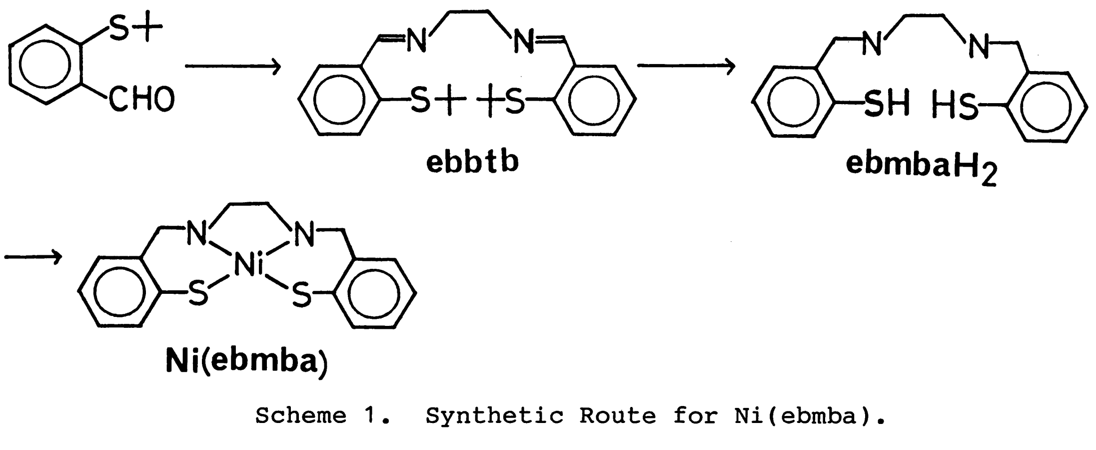
A new member was added to the class of thiolatoamine nickel complexes with square planar NiS_2N_2 geometry. Synthetic route of the compound, (N,N'-ethylenebis(*o*-mercaptobenzylaminato))nickel(II), Ni(ebmba), and the the result of X-ray structural analysis were presented. The structure and the electrochemical behavior were compared with those of (N,N'-ethylenebis(thiosalicylideneaminato))nickel(II), Ni(tsalen).

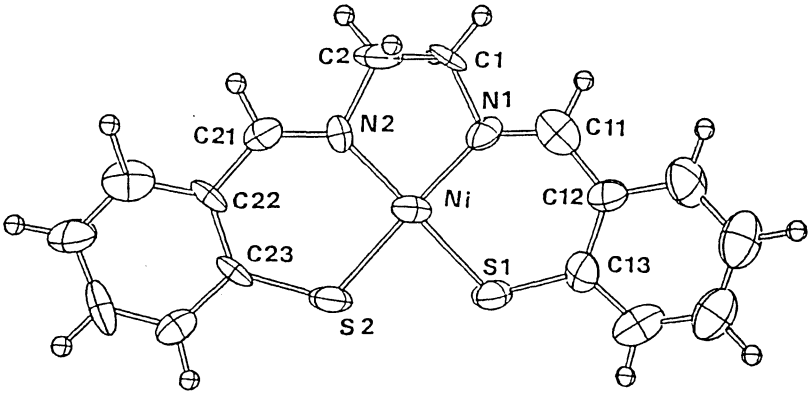
The chemistry of metal thiolates has been developed extensively in recent years. One of the increasing subgroups of this chemistry is those for platinum metals, especially for nickel.[1-10] However, the chemistry for nickel is still remained at the stage of monodentate or bidentate (aryl or alkane) thiolato nickel compounds. The examples for thiolatoamine complexes are only few.[11-13] In the preceeding paper we have presented the synthesis and the structural study of (N,N'-ethylenebis(thiosalicylideneaminato))nickel(II), Ni(tsalen),[9-10] in order to provide the example for quadridentate "imine-thiophenolate" complexes. Here we report the synthesis and the structure of the corresponding "amine-thiophenolate", (N,N'-ethylenebis(*o*-mercaptobenzylaminato))nickel(II), Ni(ebmba). **Ebmba**$^{2-}$ is the analogue of **tsalen**$^{2-}$, providing a similar $\{S_2N_2\}$ quadridentate coordination sphere. But it differs from the latter with its localized electronic structure.



Scheme 1. Synthetic Route for Ni(ebmba).

The nickel complex, Ni(ebmba), was prepared according to Scheme 1. The free base ligand, **ebmba**H_2,[14)] was derived by Burch's reduction from N,N'-ethylenebis (*o*-*t*-butylthiobenzaldimine), **ebbtb**,[15)] which was prepared from *o*-*t*-butylthiobenzaldehyde.[16)] Ni(ebmba) was obtained from the concentrated mixture of **ebmba**H_2 and $Ni(acac)_2$ in N,N-dimethylformamide.[17)] Crystals of good quality for X-ray analysis were grown slowly in dimethylsulfoxide for over three months under argon.

The structure[18)] of Ni(ebmba), Fig. 1, consists of a $Ni-N_2S_2$ pseudo square planar moiety. The distances of the component atoms from the least squares plane made up of NiS_2N_2 are 0.0006 Å (Ni), 0.1978 A (N_1), -0.2002 Å (N_2), -0.0161 Å (S_1), and 0.0322 Å (S_2). Hence, the $NiS_1S_2N_1N_2$ plane is slightly twisted around the bisector of the equilateral triangle, NiS_1S_2. The mean value of Ni-S bond length, 2.167 Å, is slightly longer than 2.157 Å of Ni(tsalen).[10)] Whereas, the Ni-N distance of Ni(ebmba), 1.945 Å, is longer than 1.86 Å of Ni(tsalen). Eventually, the chromophore of Ni(ebmba) is expanded more than that of Ni(tsalen), especially at the moiety of Ni-N-C and Ni-N=C. This structural difference reflexes electronic structure. Namely, **ebmba**$^{2-}$ is devoid of such a strong Ni(d_π)-N(p_π, -CH=N-) interaction (or the back donation) as Ni(tsalen). With respect to the strength of Ni-S bond itself, both compounds are almost the same.



$Ni-N_2$, 1.941; $Ni-N_1$, 1.949; $Ni-S_1$, 2.1639; $Ni-S_2$, 2.170; S_1-C_{13}, 1.765; S_2-C_{23}, 1.750; N_1-C_1, 1.481; N_1-C_{11}, 1.482; N_2-C_{21}, 1.487; N_2-C_2, 1.487; C_1-C_2, 1.488; $C_{11}-C_{12}$, 1.488; $C_{12}-C_{13}$, 1.404.

Fig. 1. An ORTEP drawing at the 50% probability level of thermal ellipsoids of the structure of Ni(ebmba), and the selected bond distances (Å).

In spite of the structural resemblance, the cyclic voltammogram of Ni(ebmba) was far different from that of Ni(tsalen). The latter exhibited a quasi-reversible Ni^{2+}/Ni^{+} redox couple at -1.36 V and an irreversible anodic peak at +1.00 V (vs. Ag^{+}/Ag, in DMSO). These peak positions are abnormally high comparing with ordinary thiolato nickel complexes.[1-5)] In addition, the reversibility of Ni^{2+}/Ni^{+} couple is not observed in ordinary thiolato nickel(II) compounds. In contrast, the electrochemical behavior of Ni(ebmba) was reasonable as a thiolato nickel complex, showing an irreversible anodic peak at +0.35 V and a cathodic at -1.815 V for Ni^{3+}/Ni^{2+} and Ni^{2+}/Ni^{+}, respectively. This is also explained by the presence or absence of the delocalized electronic structure, which affects the electron density of the central metal, as well as the stability of the reduced state.

The presence of nickel atom in some enzymes is now established. Nickel ions in hydrogenases[19-24)] and CO dehydrogenase[25)] are surrounded by several sulfur atoms.[21,22,25] Although there has been no evidence for that these nickels are ligated to nitrogen atom in the enzymes,[22,23] the possibility can not be denied.[26] It would be necessary to synthesize the complexes not only with pure thiolates but also with aminethiolates in order to accumulate the basis for understanding the redox behavior[5,19,20,25] and to realize the interaction between nickel and the iron-sulfur clusters,[20,22] considering the difficulty of isolating nickel/polythiolate systems.[27]

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14) **ebtbt**: Anal. Found: C, 69.24; H, 7.86; N, 6.47%. Calcd for $C_{24}H_{32}N_2S_2$: C, 69.85; H, 7.82; N, 6.79%. ^{1}H NMR ($CDCl_3$) δ ppm 1.21 (s, 18H, Bu^t), 4.01 (s, 4H, en), 7.22 - 8.12 (8H, ring), 9.08 (s, 2H, -CH=N-).

15) **ebmbaH**$_2$: Anal. Found: C, 50.67; H, 5.91; N, 7.26%. Calcd for $C_{16}H_{20}N_2Cl_2S_2$ (**ebmbaH**$_2$$\cdot$2HCl): C, 50.92; H, 5.88; N, 7.42%. ^{1}H NMR (CD_3SOCD_3) δ ppm 3.51 (bs, 4H, en), 4.12 (bs, 4H, benzyl), 6.92 – 7.42 (8H, ring), 7.98 — 10.10 (bs, 4H, -NH and -SH).

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17) Ni(ebmba): Anal. Found: C, 52.92; H, 4.98; N, 7.70%. Calcd for $C_{16}H_{18}N_2NiS_2$: C, 53.21; H, 5.02; N, 7.76%. ^{1}H NMR (CD_3SOCD_3) δ ppm 2.10 - 3.78 (8H, benzyl and en), 4.34 - 4.84 (2H, -NH), 6.56 - 7.44 (8H, ring).

18) Crystal data: for (N,N'-ethylenebis(*o*-mercaptobenzylaminato)nickel(II), M =

361.15, monoclinic, space group P21/c, a=13.324(5), b=7.9263(8), c=15.262(3) Å, β=101.23(2)°, V=1581.0(7) $Å^3$, D_c=1.52 g·cm^{-3}, μ(Mo-Kα)=14.70 cm^{-1}, Z=4. λ= 0.71069 Å (Graphite-monochromated), ω — 2θ scan up to θ=65.2 degree. R=0.037 and R_w=0.047 for 3433 reflections with I>3σ(I) collected at 23 on a Rigaku AFC5R diffractometer. Refined by full-matrix least-squares method.

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26) The extracted FT peak of the EXAFS of *D. gigas* hydrogenase[19)] seems to exhibit Ni-N(O) bond as an shoulder in the Ni-S main peak.

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