1984 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1984—1990(1993)* [Vol. 66, No. 7

Syntheses and Structures of NiS_2N_2 Compounds. [*N,N'*-Bis(*o*-mercaptobenzyliden)ethylenediaminato]nickel(II), Ni(tsalen), and [*N,N'*-Bis(*o*-mercaptobenzyl)ethylenediaminato]nickel(II), Ni(ebmba)

Takeshi YAMAMURA,* Makoto TADOKORO, Koji TANAKA, and Reiko KURODA†
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162
† Department of Chemistry, Faculty of Arts and Science, The University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo 153

(Received January 20, 1993)

The syntheses, structures, absorption spectra, and redox potentials of Ni(tsalen), H_2tsalen=*N,N'*-bis(*o*-mercaptobenzyliden)ethylenediamine, and Ni(ebmba), H_2ebmba=*N,N'*-bis(*o*-mercaptobenzyl)ethylenediamine, are described. Ni(tsalen) was prepared directly from *N,N'*-bis(*o*-*t*-buthylthiobenzyliden)ethylenediamine, from which H_2ebmba and, subsequently, Ni(ebmba) were also prepared. The crystal data for these two complexes are as follows: 1) Ni(tsalen); space group $Pna2_1$ with the unit-cell dimensions a=8.929(1), b=22.603(2), c=7.484(1) Å, Z=4, 2) Ni(ebmba); space group $P2_1/c$, a=13.324(5), b=7.9263(8), c=15.262(3) Å, β=101.23(2)°. Ni(tsalen) and Ni(ebmba) adopt squareplanar geometries with average Ni–S distances of 2.157 and 2.165 Å, respectively. The Ni–N distances of these complexes are 1.85(5) and 1.945 Å, respectively. These values, as well as the redox potentials and absorption maxima, ware compared with those of another type of NiS_2N_2 compound, $[Ni(ebtsa)]^{2-}$; H_4ebtsa=*N,N'*-bis(*o*-mercaptobenzoyl)ethlenediamide.

Although mononuclear nickel complexes with S_2N_2 coordination spheres are already recognized as being classic, they are still worthwhile studying, since they provide not only references for understanding the inorganic aspects of the nickels in hydrogenases (H_2-ases),[1] but also the starting point for model systems of H_2-ases, according to the current scope.

Tsalen^{2-},[2—7] [*N,N'*-bis(*o*-mercaptobenzyliden)ethylenediaminate]$^{2-}$, is a kind of thiophenolate ligand which belongs to S_2N_2 mixed donor systems. It realizes a typical square-planar environment and, thereby, forms an effective structural group, like its oxygen correspondent: salen^{2-}, [*N,N'*-bis(*o*-hydroxybenzyliden) ethylenediaminate]$^{2-}$. Thus, to date, saveral papers have been reported on the syntheses,[2,3b,3d,4b,4e,5a—5f,6] structures,[2,3b,3d,4a] magnetisms,[3a,3c,3d,6b] electronic structures,[2,3a—3d,4c,4d,5c,6b] redox properties,[2,3b,4c] and comparisons with M(salen) complexes (M; Fe,[3c] Co,[4a,4d] Cu[6b]). However, in spite of its importance, papers concerning tsalen complexes have been unexpectedly few, probably due to the difficulty to carry out H_2tsalen syntheses.[3a,4b] Recently, we briefly reported on a new way to obtain Ni(tsalen) and a structural analysis.[7] Subsequently, we added to the S_2N_2 group Ni(ebmba), ebmba^{2-}=[*N,N'*-bis(*o*-mercaptobenzyl)ethylenediamidate]$^{2-}$,[8] the reduced analog of Ni(tsalen). $(NEt_4)_2$[Ni(ebtsa)],[9] ebtsa^{4-}=[*N,N'*-bis(*o*-mercaptobenzoyl)ethylenediamidate]$^{4-}$,[10] presented by Kruger and Holm concerning nickels in H_2-ases, also belongs to the S_2N_2 group as was clarified by X-ray crystallography.[11] Although these three compounds have common thiophenolate groups, the electronic features around the nitrogens are different from each other (Fig. 1). Here, we wish to report on a comparison of the three compounds in terms of this difference in electron delocalization, as well as details concerning syntheses and structural analyses of Ni(tsalen) and Ni(ebmba).

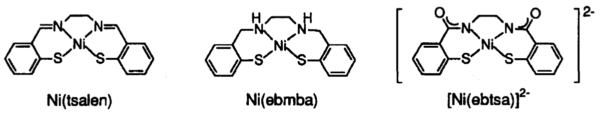

Fig. 1. Ni(tsalen); [*N,N'*-bis(*o*-mercaptobenzyliden)-ethylenediaminato]nickel(II), Ni(ebmba); [*N,N'*-bis-(*o*-mercaptobenzyl)ethylenediaminato]nickel(II), and $[Ni(ebtsa)]^{2-}$; $\{$[*N,N'*-bis(*o*-mercaptobenzoyl)ethylenediamidato]nickelate(II)$\}^{2-}$.

Experimental

Preparation of Compounds. Ebbtb, *N,N'*-bis(*o*-*t*-butylthiobenzyliden)ethylenediamine (**1**), was obtained by reacting ethylenediamine with *o*-*t*-butylthiobenzaldehyde, which was derived from *o*-nitrobenzaldehyde.[12] Ni(tsalen) (**2**) was prepared directly from this protected Schiff base, ebbtb. H_2ebmba (**3**) was prepared from ebbtb by treating it with Na/liq. NH_3. Ni(ebmba) (**4**) was synthesized by the reaction of H_2ebmba and $Ni(acac)_2\cdot 2H_2O$ (Fig. 2). All of the preparations for the deprotected thioles or thiolates were conducted under an argon atmosphere. The solvents used for complexation were dried on appropriate drying agents and degassed prior to use.

ebbtb (1): 3.11 g (52 mmol) of ethylenediamine was added to a 150 ml benzene solution containing 20.8 g (107 mmol) of *o*-*t*-butylthiobenzaldehyde, and refluxed for 30 min. The reaction mixture was cooled down to r.t., and dried over $MgSO_4$ overnight. The solvent was removed and the residue was recrystallized from hexane. Yield 17.4 g (81%). Found: C, 69.24; H, 7.86; N, 6.47%. Calcd for $C_{24}H_{32}N_2S_2$: C, 69.90; H, 7.77; N, 6.80%. ^{1}H NMR ($CDCl_3$) δ=1.21 (18H, s, *t*-BuS), 4.01 (4H, s, NCH_2CH_2N), 7.20—7.60, 7.89—8.12 (8H, ring), and 9.08 (2H, s, CH=N).

Ni(tsalen) (2): 7.51 g (18.20 mmol) of ebbtb (**1**) was mixed with 4.33 g (18.20 mmol) of $NiCl_2\cdot 6H_2O$ in 60 ml of refluxing EtOH. The solution's color changed immediately from dark green to dark brown, and formed golden mica within 5 min. After the reaction had been continued

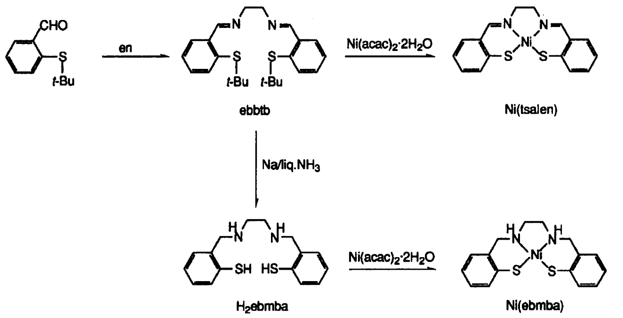

Fig. 2. Synthetic routes for Ni(tsalen) and Ni(ebmba). ebbtb; *N,N'*-bis(*o*-*t*-butylthiobenzyliden)ethylenediamine.

for an additional 6 h for completion, it was cooled to −20 °C. The crystals were collected, washed with water several times and dried in vacuo. The crude yield was 4.29 g (36%). Recrystallyzed from Me_2SO/MeOH (30 ml/10 ml) mixed solvent (Yield 47%), or CH_2Cl_2. Found; C, 53.62; H, 3.91; N, 7.83%. Calcd for $C_{16}H_{14}N_2S_2Ni$; C, 53.81; H, 3.95; N, 7.84%. ^1H NMR (Me_2SO-d_6) δ=3.72 (4H, s, NCH_2CH_2N), 6.96—7.56 (8H, ring), and 8.52 (2H, s, CH=N).

H_2ebmba·2HCl (3): 7.70 g (18.7 mmol) of ebbtb was dissolved into 50 ml of liquid ammonia. To this solution, 4.24 g (184.4 mmol) of sodium metal was added in small portions until a blue color was attained. After the reaction was completed, excess sodium was quenched by a minimum-amount of NH_4Cl. The ammonia was removed. Dissolution of the white residue into an aqueous hydrochrolic acid, which was finally adjusted at pH ca. 1 in 150 ml in an ice bath, resulted in white precipitates. These were collected and redissolved into the sodium hydroxide solution at pH ca. 12. Treatment of this solution with 10 g of NaCl gave an orange-colored impurity, which was then removed. The pH of the filtrate was again lowered to pH ca. 1 in order to deposit the desired compound. This removal of the orange impurity was repeated twice. The final precipitates were washed with a 400 ml of acidic water (pH 3—4), then dried in vacuo at 70 °C. Yield 5.31 g (75.4%). Found: C, 50.67; H, 5.91; N, 7.26%. Calcd for $C_{16}H_{20}N_2Cl_2S_2$: C, 50.92; H, 5.88; N, 7.42%. ^1H NMR (Me_2SO-d_6) δ=3.51 (4H, NCH_2CH_2N), 4.12 (4H, $PhCH_2$–), 6.96—7.42 (8H, ring) and 7.98—10.10 (4H, NH and SH).

Ni(ebmba) (4): 0.5 g (1.32 mmol) of H_2ebmba (**2**) was dissolved in 25 ml of dimethylformamide (DMF). 0.39 g (1.32 mmol) of $Ni(acac)_2 \cdot 2H_2O$ was added to this solution; the reaction mixture was stirred for 2 d at room temperature. The solution was concentrated. The resulting dark-blue crystals were filtered, washed with 40 ml of acetone twice, and dried in vacuo. Yield 0.20 g (50%). Found: C, 52.92; H, 4.98; N, 7.70%. Calcd for $C_{16}H_{18}S_2S_2Ni$: C, 53.21; H, 5.02; N, 7.76%. ^1H NMR (Me_2SO-d_6) δ=2.10—3.78 (8H, $PHCH_2$ and NCH_2CH_2N), 4.34—4.84 (2H, NH), and 6.56—7.40 (8H, ring).

Physicochemical Measurements. Cyclic voltammetry and differential pulse polarography were observed with a Yanaco P-1100 polarographic analyzer. The absorption spectra were recorded on Hitachi 228A and Hitachi 3400 spectrophotometers. ^1H NMR data were recorded on JEOL FK-100 and GSX-500 spectrometers.

Single-Crystal X-Ray Analyses. X-Ray photographs were taken to determine crystal classes; accurate cell dimensions were determined by a least-squares method for 25θ values measured on diffractometers. Intensity data were collected on rotating anode diffractometers (Enraf Nonius CAD4 for Ni(tsalen) and Rigaku AFC 5R for Ni(ebmba)), employing the ω–2θ scan mode over the ranges $2.0 \leq 2\theta \leq 60.0°$ (the former) and $1.5 \leq 2\theta \leq 65.2°$ (the latter), using Mo $K\alpha$ radiation. Lorentz and polarization corrections as well as empirical absorption and extinction corrections were applied.

The structures were solved by standard Patterson and Fourier techniques and refined on F by a full-matrix least-squares method.

Ni(tsalen): Only two hydrogen atoms (H(C11)) and H(C21)) were apparent in the difference Fourier map. The positions of the others were calculated by assuming ideal geometries. The positional and thermal isotropic parameters of all the hydrogen atoms were not refined; 2337 unique reflections were observed, out of which 1238 with $I \geq 3\sigma(I)$ were used in the structure determination. Anisotropic thermal parameters were assumed for the nonhydrogen atoms. The largest peak in the final difference Fourier map was 0.98 e$Å^{-3}$ near to the Ni atom. The maximum shift error was 0.01. The final R and R_w were 0.078 and 0.084, respectively, with $w=1/\delta(F)2$. The details are summarized in Table 1. The structure was solved[13)] using an Enraf Nonius/SDP program system on a microVax II computer at the Institute for Molecular Science, Okazaki.

Ni(ebmba): All of the hydrogen atoms were located in difference Fourier maps and their positional parameters were included in the refinement. Anisotropic and isotropic thermal parameters were assumed for the nonhydrogen and hydrogen atoms, respectively; 6121 unique reflections were measured, out of which 3433 with $I \geq 3\sigma(I)$ were used in the structure determination. Further details concerning the data collection and structure refinement are summarized in Table 1. The structure was solved using the Rigaku/MSC TEXAN program system on a microVax II computer at the Haijima factory. The largest peak in the final difference Fourier map was 0.608 e$Å^{-3}$ near to the Ni atom. The maximum shift/error was 0.04 for one of the hydrogen atoms. The final R and R_w were 0.037 and 0.047, respectively, with $w=1/\delta(F)^2$.

Results and Discussion

Structure. Structure of Ni(tsalen): Ni(tsalen) crystallized in the orthorhombic form from dichloromethane. The space group was $P_{na}2_1$. Selected bond lengths and angles are summarized in Tables 2 and 3. An ORTEP drawing is shown in Fig. 3. The molecule on Ni(tsalen) adopts square-planar geometry, a characteristic to analogs of salen complexes. The deviations of Ni, N(1), N(2), S(1), and S(2) atoms from the least-squares S_2N_2 plane are −0.0079, −0.0337, −0.0336, −0.0296, and 0.0295 Å, respectively. Hence, the NiS_2N_2 unit is slightly distorted from the square-planar geometry. Unlike many salen complexes, which exhibit flat $Ni(OCCCN)_2$ centers, Ni(tsalen) is eccentrically bent at S(1)C(11) line, but a fairly good copla-

Table 1. Summary of Crystal Data, Intensity Collection, and Structural Parameters for the Nickel Complexes

Quantity	Ni(ebmba)	Ni(tsalen)
Diffractometer	RIGAKU-AFC5R	ENRAF-NONIUS CAD4
Formula	$C_{16}H_{18}N_2NiS_2$	$C_{16}N_{14}N_2NiS_2$
Formula weight	361.5	357.14
Crystal system	Monoclinic	Orthorhombic
Lattice parameters		
a/Å	13.324(5)	8.929(1)
b/Å	7.9263(8)	22.603(2)
c/Å	15.262(3)	7.484(1)
β/°	101.23(2)	
V, Å^3	1581.0(7)	1510.4(5)
$F(000)$	752	736
Space group	$P2_1/c$	$Pna2_1$
Z value	4	4
D_c g cm^{-3}	1.52	1.570
Crystal dimensions/mm	—	0.15×0.10×0.49
Radiation/nm	Mo $K\alpha$ (λ=0.7107) Graphite Monochromated	Mo $K\alpha$ (λ=0.7107) Graphite Monochromated
Abs. coeff., μ/cm^{-1}	14.70	15.48
Temp/°C	23	23
Scan speed/° min^{-1}	4	4.12
Scan range/°	$1.5<2\theta<65.2$	$2.0<2\theta<60.0$
No. of unique reflections	6121	2337
No. of observations ($I>3.00\sigma(I)$)	3433	1238
No. of variables	244	190
Residuals: R; R_w	0.037; 0.047	0.078; 0.084
Maximum shift in final cycle	0.04	0.01
Largest peak in final diff. map, e Å^{-3}	0.61	0.98

narity is conserved between the central NiS_2N_2 plane and one of the o-mercaptobenzylidenaminate(2) planes (Fig. 3). Two of the least-squares planes containing nickel, NiS(2)N(2)C(21)C(23)C(22) and NiS(1)N(1)C(11)C(13)C(12), are thus inclined to the NiS(1)S(2)N(1)N(2) plane with dihedral angles of 3.63 and 15.70°, respectively. The benzene rings connected to NiS(2)N(2)C(21)C(23)C(22) and NiS(1)N(1)C(11)C(13)C(12) are inclined at 3.69 and 26.19°, respectively, to the N_2S_2 plane. A deviation from bilateral symmetry is also seen between the two Ni–S bond lengths, Ni–S(1)=2.174(5) Å and Ni–S(2)=2.139 Å. However, this asymmetry does not affect the C=N bond lengths (1.30(2) and 1.29(2) Å). This eccentric bending may be the result of crystal packing. Fianlly, the ethylene bridge of this compound is in the *gauche* position.

Table 2. Selected Bond Distances (Å) of Ni(tsalen) and Ni(ebmba) [a)]

Bonding	Ni(tsalen)	Ni(ebmba)
Ni–S1	2.139(5)	2.170(1)
Ni–S2	2.174(5)	2.1639(9)
Ni–N1	1.85(1)	1.949(2)
Ni–N2	1.86(1)	1.941(2)
S1–C13	1.70(2)	1.765(3)
S2–C23	1.73(2)	1.750(3)
C11–C12	1.43(3)	1.488(4)
C21–C22	1.44(2)	1.493(4)
N1–C11	1.29(2)	1.482(4)
N2–C21	1.30(2)	1.487(4)
N1–C1	1.51(2)	1.481(3)
N2–C2	1.51(2)	1.487(4)
C1–C2	1.47(3)	1.488(5)
C12–C13	1.47(2)	1.404(4)
C22–C23	1.41(2)	1.401(5)

a) Numbers in parentheses are estimated standard deviations in the least significant digits.

Structure of Ni(ebmba): Ni(ebmba) crystallized in monoclinic. The space group is $P2_1/c$. Its NiS_2N_2 unit is pseudo square planar (Fig. 4). The bond lengths and angles are listed in Tables 2 and 3, respectively. The distances of the component atoms from the NiS_2N_2 least-squares plane are 0.0006 (Ni(1)), 0.1978 (N(1)), −0.2002 (N(2)), −0.0161 (S(1)), and 0.0322 (S(2)) Å. The Ni(1)S(1)S(2)N(1)N(2) plane is slightly twisted around the bisector of the equilateral triangle,

Table 3. Selected Bond Angles (°) of Ni(tsalen) and Ni(ebmba) a)

Bond angle			Ni(tsalen)	Ni(ebmba)
Atom1	Atom2	Atom3	Angle	Angle
S1	Ni	N1	94.2(4)	95.83(7)
S1	Ni	N2	178.6(4)	173.29(7)
S1	Ni	S2	83.8(3)	83.13(4)
S2	Ni	N1	176.9(4)	173.27(7)
S2	Ni	N2	96.0(5)	94.87(8)
N1	Ni	N2	86.1(5)	86.9(1)
Ni	S1	C13	111.3(6)	111.92(9)
Ni	S2	C23	113.4(5)	111.6(1)
Ni	N1	C1	111.(1)	106.9(2)
Ni	N1	C11	133.(1)	120.1(2)
Cl	N1	C11	115.(1)	109.6(2)
Ni	N2	C2	112.(1)	108.9(2)
Ni	N2	C21	133.(1)	118.5(2)
C2	N2	C21	115.(1)	110.9(2)
N1	C1	C2	103.(1)	107.5(2)
N2	C2	C1	108.(1)	107.2(2)
N1	C11	C12	127.(2)	114.5(2)
S1	C13	C12	125.(1)	122.9(2)
C11	C12	C13	123.(2)	121.8(2)
N2	C21	C22	130.(2)	112.2(2)
S2	C23	C22	125.(1)	123.1(2)
C21	C22	C23	122.(1)	121.3(3)

a) Numbers in parentheses are estimated standard deviations in the least significant digits.

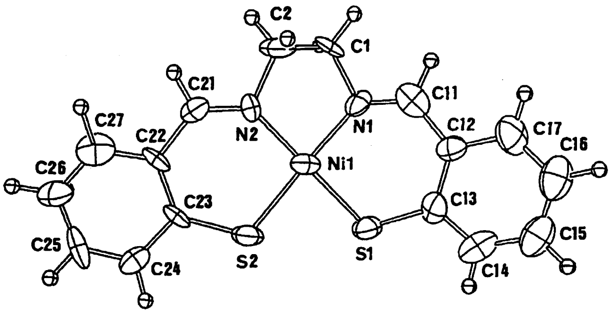

Fig. 3. Structure of Ni(tsalen) with atom numberings showing 50% probability of thermal ellipsoids.

Ni(1)S(1)S(2). The dihedral angles between the NiS_2N_2 least-squares plane and NiS(1)N(1)C(11)C(12)C(13), NiS(2)N(2)C(21)C(22)C(23), NiN(1)N(2)C(1)C(2), C(12)C(13)C(14)C(15)C(16)C(17), ring 1, and C(22)C(23)C(24)C(25)C(26)C(27), ring 2 are 4.04, 1.35, 5.51, 23.66, and 25.27°, respectively. Thus, in contrast to Ni(tsalen), Ni(ebmba) conserves good planarity in the first coordination sphere and its adjacent area. However, the two benzene rings are bent to this central plane with fairly large dihedral angles, due to bending at the methylene bridges of the benzyl parts. The ethylene bridge is in the *gauche* position. Similarly to Ni(salen)14) and [Fe(tsalen)Cl],3d) two Ni(tsalen) molecules are paired in the unit cell. However, there was no evidence for a tight binding of the pairing molecules due to a mutual coordination of the nitrogen atoms to the neightboring nickels from the axial direction, as had been observed for [Co(tsalen)],4a) or in the stacked crystal structures of nickel complexes with deprotonated α,β-dionedioximes: bis-(1,2-dimethylglyoximate)nickel(II)15) and bis-(glyoximate)nickel(II).16) The pair shows a stepped configuration as found for many salen complexes.3d,17,18)

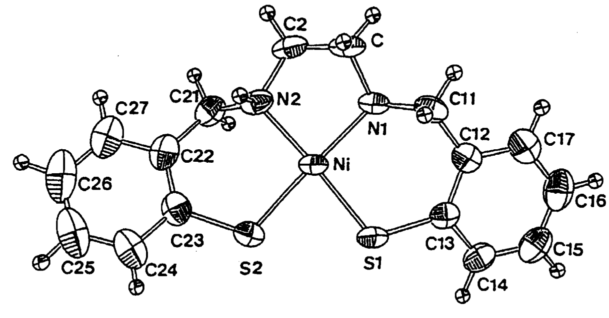

Fig. 4. An ORTEP drawing of Ni(ebmba) showing 50% probability of thermal ellipsoids. The atom numbering is unified as in Fig. 3.

Structural Comparison: The Ni–S(O), Ni–N and C=N bond lengths of Ni(ebmba), Ni(tsalen), $[Ni(ebtsa)]^{2-}$,11) and Ni(salen)14) are compared in Table 4. Although a similar table was already presented by Dutton, Fallon, and Murray,11) their paper lacks a detailed comparison. It is impossible to find any significant difference among the average Ni–S bond lengths for Ni(tsalen), $[Ni(ebtsa)]^{2-}$, and Ni(ebmba) (2.157, 2.155, and 2.167 Å, respectively), whereas it is easy for the Ni–N lengths. They are 1.855, 1.90, and 1.945 Å, respectively. Thus, the deviation among the three compounds is remarkable regarding the Ni–N bond length rather than in Ni–S. The Ni–N bond-length order reflects the nature of the bonds in the three compounds (Fig. 1), among which Ni(tsalen) and $[Ni(ebtsa)]^{2-}$ have a large delocalized electronic structure over nitrogen and sulfur (see the C=N and CS bond lengths in Table 4), whereas Ni(ebmba) does not. Thus, although the former cases enable Ni→N π-backdonation, the latter does not. The Ni–N bond lengths of Ni(tsalen) are, however, only slightly deviated from those of Ni(salen). Therefore, the delocalization is not strongly dominated by the sulfur or oxygen.

Synthesis of Ni(tsalen). Several reports concerning Ni(tsalen)5) and a dimethyl derivative complex5f)

Table 4. Comparison of Ni-X (X=S, O)a) and Ni-N Bond Distances (Å) for Ni(tsalen), Ni(ebmba), $[Ni(ebtsa)]^{2-}$,11) and Ni(salen)14)

Bond	Ni(tsalen)	Ni(ebmba)	$[Ni(ebtsa)]^{2-}$	Ni(salen)
Ni-X1	2.174	2.1639	2.161	1.850
Ni-X2	2.139	2.170	2.149	1.855
Ni-N1	1.85	1.949	1.90	1.853
Ni-N2	1.86	1.941	1.89	1.843

a) X=S for Ni(tsalen), Ni(ebmba), and $[Ni(ebtsa)]^{2-}$, X=O for Ni(salen).

have been published to date without including any structural analyses. As already mentioned, only four tsalen complexes have been reported along with molecular structures; $[Fe(tsalen)]_2$,[3b] Fe(tsalen)Cl,[3d] $[Co(tsalen)]_2$,[4a] and VO(tsalen).[2] Considering (a) the correspondence between tsalen and salen, (b) the recent interest in sulfur as an anionic donor, since it behaves as a strong electron donor as well as a mild π-acid,[19] and (c) the importance of metal sulfur bonds in biological systems, tsalen should be the subject of more investigations in coordination chemistry. One of the reasons for this situation lies in the synthetic route to H_2tsalen, itself, which passes through thiosalicyl aldehyde, Htsal.[3b,4b] The approaches to Htsal which have so far been examined are poor in reproducibility, as was pointed out in Ref. 3a. Furthermore, the reaction of Htsal with ethylenediamine results in an equilibrium mixture containing the iminomethylbenzenethiol Schiff base, as well as in a bridged bicyclononane impurity.[4b] A successful route to tsalen complexes passing through the useful intermediate, $[Tl_2(tsalen)]$, which was readily prepared from [Tl(tsal)] with ethylenediamine, was devised by R. J. Cozens et al.[20,21]

Our method (Fig. 2) is an extension of that of Becher and his coworkers'.[22—27] They cleaved the alkylthio groups by using Cu^{2+} to prepare copper-Schiff base complexes. Generally speaking, the alkylthio groups are cleaved by applying $Hg^{2+}(Ag^{+})$/Lewis acid conditions.[28] Considering that metal ions show Lewis acidity, the *t*-butyl group of ebbtb may generally be substituted by metal ions with or without the aid of a Lewis acid such as CF_3COOH. However, in our preliminary experiments concerning the first-row transition metal ions, only Ni^{2+} underwent a substitution reaction subsequent to a *t*-butylthio group cleavage. The other metal ions showed no such activity, even under strong Lewis acids. Attempts to isolate H_2tsalen from ebbtb by employing $Hg(CF_3COOH)_2/CF_3COOH$/anisole and H_2S failed, giving many by-products. Finally, it should be pointed out that our new route is suitable for large-scale syntheses.

Electrochemistry. The absorption maxima and the electrochemical cathodic wave positions are summarized in Table 5. The cyclic voltammograms of Ni(tsalen) and Ni(ebmba) in Me_2SO, and $[Ni(ebtsa)]^{2-}$ in DMF are depicted in Fig. 5. As can be seen here, Ni(tsalen) exhibits a quasi-reversible Ni^{2+}/Ni^{+} couple at $E_{1/2}=-1.36$ V (vs. Ag^{+}/Ag, peak separation=0.22 V), and an irreversible Ni^{3+}/Ni^{2+} couple at $E_{ap}=+1.00$ V. On the contrary, $[Ni(ebtsa)]^{2-}$ affords no Ni^{2+}/Ni^{+} couple, but a quasi-reversible Ni^{3+}/Ni^{2+} couple at $E_{1/2}=$ 0.02 V in DMF.[29] In contrast to Ni(tsalen) and $[Ni(ebtsa)]^{2-}$, the electrode processes of Ni(ebmba) are irreversible for both reduction and oxidation. The cathodic wave position (−1.81 V for Ni^{2+}/Ni^{+}) and the anodic wave position (+0.59 V for Ni^{3+}/Ni^{2+}) are 0.3—0.4 V lower than those of Ni(tsalen). These increased stabilities of Ni^{+} in Ni(tsalen) and Ni^{3+} in $[Ni(ebtsa)]^{2-}$ can be explained by their extended electronic delocalization at –C=N– and $-CON^{-}-$, respectively.

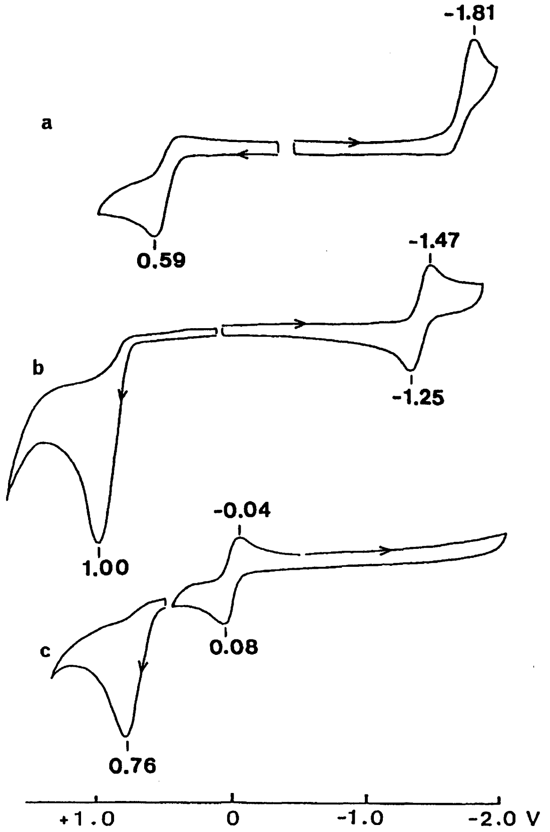

Fig. 5. Cyclic Voltammograms (100 mV s^{-1}) at 25 °C with a glassy carbon electrode (vs. Ag/AgCl, 0.1 md dm^{-3} TEAP): a) Ni(ebmba); observed in Me_2SO, b) Ni(tsalen); observed in Me_2SO, and c) $[Ni(ebtsa)]^{2-}$; observed in DMF (*N,N'*-dimethylformamide).

Both Ni^{2+}/Ni^{+} and Ni^{3+}/Ni^{2+} couples of $[Ni(ebtsa)]^{2-}$ are far more negatively shifted compared to the other compounds (Table 5). This negative shift is attributable to a strong electron donation by the amide nitrogen (N^{-}) of $ebtsa^{4-}$. Balch had compared the redox potentials of MX_4 compounds with $X=O^{-}$, S^{-}, N^{-}, and their mixed donor sets,[30] among which N^{-} was the strongest donor giving the most negative Ni^{3+}/Ni^{2+} potentials. It should be pointed that $ebtsa^{4-}$ is the sulfur analog of $ebsa^{4-}$ ($ebsa^{4-}=[$*N,N'*-bis(*o*-hydroxybenzoyl)ethylenediamidate$]^{4-}$),[9] which is one of the PAC ligands and stabilizes high oxidation states of transition metals.[31] The positive shifts of Ni^{2+}/Ni^{+} and Ni^{3+}/Ni^{2+} couples of Ni(tsalen), compared with Ni(ebmba), seem to reflect of the strong covalency of Ni–N bonding in Ni(tsalen).

The Ni^{3+}/Ni^{2+} anodic oxidation potentials of the three compounds seem to correlate with the energies of the absorption bands observed at 340—390 nm (Table 5). The three compounds exhibited electronic transition patterns which are common to the nickel ions immersed in square-planar sulfur environment.[32,33] Zerner and his co-workers calculated the electronic structure of bis(propene-3-thione-1-thiolato)nickel(II), NiPTT, by the INDO-SCF-CI method.[33] According to their calculation, which explained well the absorption spectrum of NiPTT's NiS_4 environment, the bands at 340, 386, and 376 nm observed for $[Ni(ebtsa)]^{2-}$, Ni(ebmba), and Ni(tsalen), respectively, are attributable to the transitions from $Ni(d_{xz},d_{yz})+L(\pi)$ to $L(\pi^*)$. The observed correlation between the LMCT absorption maxima and the oxidation potentials for $[Ni(ebtsa)]^{2-}$, Ni(ebmba), and Ni(tsalen) makes us expect that the highest occupied molecular orbitals (HOMO) of these compounds are $Ni(d_{xz},d_{yz})+L\pi$. This expectation agrees well with Zerner's assignment for NiPTT.

In contrast to the difference among these three NiS_2N_2 compounds, a resemblance between sulfur and oxygen correspondents is conspicuous. For example, Ni(tsalen) and Ni(salen) exhibits similar CV signals for $Ni^{2+}\rightarrow Ni^{3+}$ and $Ni^{2+}\rightarrow Ni^{+}$ redox couples (Table 5). A similar resemblance has been reported for $[Ni(ebtsa)]^{2-}$ and $[Ni(ebsa)]^{2-}$ by Kruger and Holm (Table 5). In consequence, the difference between sulfur and oxygen is not significant compared with that among amine ($ebmba^{2-}$), imine($tsalen^{2-}$), and amide ($ebtsa^{4-}$) with respect to electrochemistry. It would not be the sulfur or oxygen, but the nitrogen, which dominates the HOMO/LUMO energy levels of this series of complexes. The results of X-ray crystallography, which show that the deviation in the Ni–S bond lengths is far smaller than in the Ni–N, seems to supports this.

Nickel complexes with S_2N_2 coordination spheres are forming one possible gateway for comparative and synthetic approaches to the active site of H_2-ases, which are mononuclear and immersed in an S_xN_y environment.[34] For example, the introduction of pendant groups to NiS_2N_2 units afford extended structural models of the central nickels in H_2-ases. The cases described here provide standards for comparative studies of such extended compounds.

This work was supported by a Grant-in-Aid for Scientific Research No. 62540475 from the Ministry of Education, Science and Culture.

References

1) "The Bioinorganic Chemistry of Nickel," ed by J. R. Lancaster, Jr., VCH Publishers, New York (1988).

2) J. C. Dutton, G. D. Fallon, and K. S. Murray, *Inorg. Chem.*, **27**, 34 (1988).

3) a) P. J. Marini, K. S. Murray, and B. O. West, *J. Chem. Soc., Chem. Commun.*, **1981**, 726; b) P. J. Marini, K. S. Murray, and B. O. West, *J. Chem. Soc., Dalton Trans.*, **1983**, 143; c) P. J. Marini, K. J. Berry, K. S. Murray, and B. O. West, *J. Chem. Soc., Dalton Trans.*, **1983**, 879; d) G. D. Fallon, B. M. Gatehouse, P. J. Marini, K. S. Murray, and B. O. West, *J. Chem. Soc., Dalton Trans.*, **1984**, 2733.

4) a) G. D. Fallon and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, **32**, 97 (1976); b) M. F. Corrigan, and B. O. West, *Aust. J. Chem.*, **29**, 1413 (1976); c) M. F. Corrigan, K. S. Murray, and B. O. West, *J. Chem. Soc., Dalton Trans.*, **1977**, 1478; d) K. S. Murray and R. M. Sheahan, *J. Chem. Soc., Dalton, Trans.*, **1976**, 999; e) A. van den Bergan, M. F. Corrigan, K. S. Murray, and B. O. West, *Inorg. Nucl. Chem. Lett.*, **10**, 859 (1975); f) J. D. Fallon and B. M. Gatehouse, *Inorg. Nucl. Chem. Lett.*, **11**, 625 (1975).

5) a) E. Hoyer and B. Lorentz, *Z. Chem.*, **8**, 28 (1968); b) L. P. Olekhnovich, V. P. Kurbatov, O. A. Osipov, and L. S. Minkina, *J. Gen. Chem. USSR (Engle. Transl.)*, **38**, 2512 (1968); c) I. Bertini, L. Sacconi, and G. P. Speroni, *Inorg. Chem.*, **11**, 1323 (1972); d) H. R. Engesrth, D. R. McMillin, and E. L. Urlich, *Inorg. Chim. Acta*, **67**, 145 (1982); e) S. K. Mondal, D. S. Joardar, and K. Nag, *Inog. Chem.*, **17**, 191 (1978); f) R. C. Coombes, J. P. Costes, and D. E. Fenton, *Inorg. Chim. Acta*, **77**, 173 (1983).

6) a) G. S. Patterson, and R. H. Holm, *Bioinorg. Chem.*, **4**, 257 (1975); b) M. F. Corrigan, K. S. Murray, B. O. West, and J. R. Pilbrow, *Aust. J. Chem.*, **30**, 2455 (1977).

7) T. Yamamura, M. Tadokoro, and R. Kuroda, *Chem. Lett.*, **1989**, 1245.

8) T. Yamamura, M. Tadokoro, M. Hamaguchi, and R. Kuroda, *Chem. Lett.*, **1989**, 1481.

9) H. J. Kruger and R. H. Holm, *Inorg. Chem.*, **26**, 3645 (1987).

10) H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.*, **10**, 556 (1962).

11) J. C. Dutton, G. D. Fallon, and K. S. Murray, *Chem. Lett.*, **1990**, 983.

12) O. Meth-Cohn and B. Tarnowski, *Synthesis*, **1978**, 58.

13) "International Tables for X-Ray Crystallography," (Present Distributor D. Reidel, Dordrecht) The Kynoch Press, Birmingham (1974), Vol. IV, pp. 71—151.

14) L. M. Shkol'nikova, E. M. Yumal, E. A. Shugam, and V. A. Voblikova, *Zh. Strukt, Khim.*, **11**, 886 (1970); A. G. Manfredotti and C. Guastini, *Acta Crystallogr., Sect. C*, **39**, 863 (1983).

15) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).

16) K. Murmann and E. D. Schlenper, *Acta Crystallogr.*, **23**, 667 (1967).

17) M. Calligaris, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, **1972**, 2003.

18) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).

19) S. R. Cooper, *Acc. Chem. Res.*, **21**, 141 (1988).

20) R. J. Cozens, K. S. Murray, and B. O. West, *Aust. J. Chem.*, **23**, 683 (1970).

21) R. J. Cozens, K. S. Murray, and B. O. West, *J. Organomet. Chem.*, **27**, 399 (1971).

22) J. Becher, D. J. Brockway, K. S. Murray, P. J. Newman, and H. Toftlund, *Inorg. Chem.*, **21**, 1791 (1982).

23) J. Becher, H. Toftlund, and P. H. Olesen, *J. Chem. Soc., Chem. Commun.*, **1983**, 740.

24) J. Becher, H. Toftlund, P. H. Olesen, and H. Nissen, *Inorg. Chim. Acta*, **103**, 167 (1985).

25) J. Becher, C. E. Stidsen, H. Toftlund, and F. M. Asaad, *Inorg. Chim. Acta*, **121**, 23 (1986).

26) O. P. Anderson, J. Becher, H. Frydendahl, L. F.

Taylor, and H. Toftlund, *J. Chem. Soc., Chem. Commun.*, **1986**, 699.

27) J. Becher, *Phsophorus Sulfur Silicon*, **43**, 289 (1989).

28) T. W. Greene, "Photoactive Groups in Organic Synthesis," J. Wiley & Sons, New York (1981).

29) This work. This compound was assigned as $(NEt_4)[Ni(H_2ebtsa)](OH)$ in our previous paper (T. Yamamura, M. Tadokoro, N. Nakamura, K. Tanaka, and K. Asakura, *Bull. Chem. Soc. Jpn.*, **63**, 999 (1990)). However, this afforded the same absorption maxima as $(NEt_4)_2[Ni(ebtsa)]$ by Kruger and Holm[9)] in EtOH. They reported the half wave potential for their compound as −0.035 V (in DMF, vs. SCE), which is very close to our observation (0.02 V vs. Ag^+/Ag in DMF). The molecular structure of $(NEt_4)_2[Ni(ebtsa)]$ revealed by Dutton, Fallon, and Murray[11)] shows the existence of $[Ni(ebtsa)]^{2-}$ chromophore in the crystal. Considering these, the compound which we proposed as $(NEt_4)[Ni(H_2ebtsa)](OH)$ in the previous paper should be reassigned as $(NEt_4)(H^+)[Ni(ebtsa)]\cdot H_2O$.

30) A. L. Balch, F. Rohrscheid, and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

31) F. C. Anson, T. J. Collins, S. L. Gipson, J. T. Keech, and T. E. Kraft, *Inorg. Chem.*, **26**, 1157 (1987).

32) O. Siiman, D. D. Titus, C. D. Cowman, J. Fresco, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 2353 (1974).

33) Z. S. Herman, R. F. Kirchiner, G. H. Loew, U. T. Mueller-Westerhoff, A. Nazzal, and M. C. Zerner, *Inorg. Chem.*, **21**, 46 (1982).

34) P. A. Lindahl, N. Kojima, R. P. Hausinger, J. A. Fox, B-K. Teo, C. T. Walsh, and W. H. Orme-Johnson, *J. Am. Chem. Soc.*, **106**, 3062 (1984); R. A. Scott, S. A. Wallin, M. Czechowski, D. V. DerVartanian, J. LeGall, H. D. Peck, Jr., and I. Moura, *J. Am. Chem. Soc.*, **106**, 6864 (1984); N. R. Bastian, G. Diekert, E. C. Niederhoffer, B-K. Teo, C. T. Walsh, and W. H. Orme-Johnson, *J. Am. Chem. Soc.*, **110**, 5581 (1988); M. K. Eidsness, R. A. Scott, B. C. Pricril, D. V. DerVartanian, J. LeGall, I. Moura, J. J. G. Moura, and H. D. Peck, Jr., *Proc. Natl. Acad. Sci. U.S.A.*, **86**, 147 (1989); M. Maroney, G. J. Colpas, and C. Bagyinka, *J. Am. Chem. Soc.*, **112**, 7067 (1990); J. P. Whitehead, G. J. Colpas, C. Bagyinka, and M. J. Maroney, *J. Am. Chem. Soc.*, **113**, 6288 (1991); M. Maroney, G. J. Colpas, C. Bagyinka, N. Baidya, and P. K. Mascharak, *J. Am. Chem. Soc.*, **113**, 3962 (1991).