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Ni(II) Complexes of *N,N'*-Ethylenebis(*o*-mercaptobenzamide): A Quadridentate Thiolato Amide {S_2N_2} Ligand

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Three nickel(II) complexes with *N,N'*-ethylenebis(*o*-mercaptobenzamide), H_4ebtsa, a quadridentate {S_2N_2} ligand classified as a PAC (polyanionic chelating) ligand, were isolated. Although they were different in their apparent charges, their coordination units were revealed to be equal from their physicochemical behavior. They will be described as Ni(H_2ebtsa). EXAFS and XANES study was undertaken for one of the new compounds, and the results were compared with those for similar three NiS_2N_2 complexes, (*N,N'*-ethylenebis(*o*-mercaptobenzylidenaminato))Ni(II), (*N,N'*-ethylenebis(*o*-mercaptobenzylaminato))Ni(II) and (NEt_4)[Ni-($SPh)_4$]. From these results and a comparison with the results for [Ni(ebtsa)]$_2$, it was concluded that a square planar {S_2N_2} unit was reliable as the coordination sphere of Ni(H_2ebtsa). The character of the amide proton in the coordination unit was also studied.

Bonds between metals and amide nitrogen are known to stabilize high oxidation states[1-4] or to lower the oxidation potential.[5] H_4ebtsa (Fig. 1),** first prepared by Tanaka about 20 years ago,[6] is the mercapto correspondent of *N,N'*-ethylenebis(salicylamide)[7,8] and belongs to the family of amide type PAC (polyanionic chelating) ligands,[1-3] which have been shown to stabilize the high valent states of manganese ($Mn^{4,5+}$),[4] osmium ($Os^{4,6+}$),[1] copper (Cu^{3+}),[2] and cobalt (Co^{4+}).[3]

Recently, Cruger and Holm[8] have reported the synthesis of $(NEt_4)_2$[Ni(ebtsa)] and shown the trap of Ni^{3+} in an electrolytic EPR cell. We ourselves also have previously reported, independently, the synthesis of (NEt_4)[Ni(H_2ebtsa)](OH) and the generation of Ni^{3+} in solution.[9] In the recent trend to synthesize high-valent complexes,[1-4,8] Ni(III) occupies a noble situation in the context of bioinorganic chemistry. Its study includes the background chemistry of the Ni^{3+} sites of uptake hydrogenases,[10-12] which oxidize H_2. In spite of this situation of Ni/ebtsa, the details of nickel/ebtsa synthesis has not yet been published. Here, we wish to report the isolation of three Ni/ebtsa complexes, the study of their oxidation behavior, and the ionization of the amide proton.

The compounds represented here are two types of nickel/ebtsa compounds, which are different in apparent charge from each other and also from that reported by Cruger and Holm.[8] Although these compounds seemed to form a class described as $[Ni(H_n ebtsa)]^{(2-n)-}$ [n=0, 1, 2) on the basis of the analytical and ^{1}H NMR data, the comparative studies of these compounds with Ni(tsalen),*** Ni(ebmba),*** and [Ni(H_2ebtsa)]$_2$[13] by using UV-vis. and XAFS (XANES and EXAFS) measurements have revealed that they have the same coordination unit, Ni(H_2ebtsa), with a square planar NiS_2N_2 coordination sphere. Their IR (in solid) and NMR (in solution) signals were compared with those of $(NEt_4)_2$ [Ni(H_2tsa)$_2$](OH)$_2$,*** in order to reveal the ionization character of the amide hydrogen of Ni(H_2ebtsa). It was impossible to obtain evidence for a steady N-H bond in the coordination unit.

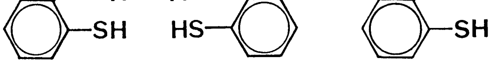

Fig. 1. Right; H_4ebtsa=*N,N'*-ethylenebis(*o*-mercaptobenzamide) or *N,N'*-ethylenebis(thiosalicylamide).
Left; H_3tsa=*o*-mercaptobenzamide or thiosalicylamide.

Experimental

Preparation of Compounds. All the treatment of the materials including thiol or thiolate moieties were conducted under an argon atmosphere. The solvents for complexation were dried on appropriate drying agents and degassed prior to use. The phenyl *o*-mercaptobenzoate (thiosalol) was prepared according to Mayer's method.[14] Ni(tsalen) and Ni(ebmba) were prepared by the published methods.[15,16]

H_4ebtsa: 25.9 g (0.113 mol) of thiosalol was dissolved in 250 cm^3 of xylene, into which 3.6 g (0.0534 mol) of ethylenediamine was added slowly with vigorous stirring under reflux. The reaction was continued for a further 12 h. The reaction mixture was cooled to room temperature. The resulting insoluble yellow material was collected by filtration, washed with three 50 cm^3 portions of xylene, and dried in vacuo. This material was washed further with three 100 cm^3 portions of hot EtOH. The residue was then treated with 100 cm^3 of EtOH at room temperature, and the white suspension observed in the solution was removed by

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** H_4ebtsa=*N,N'*-ethylenebis(*o*-mercaptobenzamide) or *N,N'*-ethylenebis(thiosalicylamide).

*** H_3tsa=*o*-mercaptobenzamide or thiosalicylamide.
H_2tsalen=*N,N'*-ethylenebis(*o*-mercaptobenzylidenamine) or *N,N'*-ethylenebis(thiosalicylidenamine).[15]
H_2ebmba=*N,N'*-ethylenebis(*o*-mercaptobenzylamine).[16]

decantation. This procedure was repeated several times until the white suspension was not observed. The second crop was recovered from the hot, 300 cm^3 EtOH washings. Yield: 11.8 g (67%). This material was used for the next reaction without further purification. Recrystallized from DMF. Found: C, 57.54; H, 4.89; N, 8.42%. Calcd for $C_{16}H_{16}O_2N_2S_2$: C, 57.81; H, 4.85; N, 8.43%. ^{1}H NMR (DMSO-d_6) δ=8.51 (2H, s, -CONH-), 7.85—7.05 (8H, ring), 5.36 (2H, s, -SH), 3.40 and 3.44 (4H, s, -NCH_2CH_2N-).

H_3tsa: 18 g (78.2 mmol) of thiosalol was dissolved in 300 cm^3 of aqueous ammonia solution (concd) and stirred for 4 days. The solution was heated to remove the ammonia and then distilled under reduced pressure. The sublimation of the residue gave ca. 11 g of a milky white powder, which was then recrystallized from xylene, washed with small amount of ether, and dried in vacuo. White needles. Yield: 7.8 g (72%). Found: C, 55.04; H, 4.67; N, 9.03; S, 20.75%. Calcd for C_7H_7NOS: C, 54.88; H, 4.61; N, 9.14; S, 20.93%. ^{1}H NMR (DMSO-d_6) δ=8.00 (2H, d, -$CONH_2$), 7.69—7.08 (4H, 4H), 5.43 (1H, s, -SH).

$(NEt_4)[Ni(H_2ebtsa)](OH)$, 1: 3.06 mmol of Li_4ebtsa was prepared by dissolving 0.085 g (12.2 mmol) of lithium metal and 1.02 g (3.06 mmol) of H_4ebtsa in MeOH. The MeOH was then removed completely. The Li_4ebtsa was suspended in 10 cm^3 of acetonitrile, to which a 50 cm^3 of acetonitrile solution containing 1.9 g of $(NEt_4)_2NiBr_4$ was added slowly. The reaction mixture was stirred for more than 2 h under reflux and then filtered to remove the supernatant. The precipitate was washed with another 50 cm^3 of the refluxing acetonitrile. The dissolution of the residue in acetonitrile/MeOH (1 : 1) led to the appearance of a green-white suspension of impurities, which was then filtered off. The solvent was distilled off from the filtrate. This treatment to remove the green-white suspension in acetonitrile/MeOH was repeated several times. The solvents were then removed, and the residue was dried in vacuo. Yield: 1.5 g (75%). Found: C, 53.50; H, 6.44; N, 7.44%, Cl trace amount. Calcd for $C_{24}H_{35}N_3O_3S_2Ni$: C,53.74; H, 6.58; N, 7.83%. ^{1}H NMR (DMSO-d_6) δ=1.04—1.22 (12H, t, cation's -CH_3), 3.00 (4H, s, -NCH_2CH_2N-), 3.09—3.30 (8H, q, cation's -CH_2), 6.53—6.79 (4H, ring proton), 7.00—7.09 (2H, ring proton), 7.81—7.90 (2H, ring proton).

$(PPh_4)[Ni(H_2ebtsa](OH)(H_2O)$, 2: 6.02 mmol of Li_4ebtsa was prepared from 2.00 g (6.02 mmol) of H_4ebtsa and 0.17 g (24.1 mmol) of lithium in 60 cm^3 of MeOH. After the solvent had been removed, and the residue dried well under a vacuum, 40 cm^3 of acetonitrile was introduced into the flask, into which an acetonitrile solution (50 cm^3) containing 5.29 g (6.02 mmol) of $(PPh_4)_2[NiCl_4]$ was then added drop by drop under a reflux. After 1 h, white precipitates appeared. These were filtered off, and the solvent was removed from this filtrate. The residue was redissolved in a 150 cm^3 of acetonitrile, and the brown precipitates which appeared again in the solution were filtered off. The filtrate was mixed with a 75 cm^3 of acetone, and left at −10 °C for 2 days. The fine powders which then appeared in the solution were filetered off, and the filtrate was allowed to stand for 2 weeks in a refrigerator (−10 °C). The green crystals which grew in the flask were collected, dried in vacuo, and recrystallized from acetonitrile three times. Yield: 1.2 g (26.6%). Found: C, 62.89; H, 4.53; N 3.70%, Cl trace amount. Calcd for $C_{40}H_{37}O_4N_2NiPS_2$: C, 62.92; H, 4.88; N, 3.67%. ^{1}H NMR (DMSO-d_6) δ=3.02 (4H, s, -NCH_2CH_2N-), 6.41—6.79, 6.84—7.12 (6H, ring proton/ligand), 7.48—8.24 (22H, ring proton/ligand and cation).

$[Ni(H_2ebtsa)]2(CH_3OH)2(H_2O)2(CH_3COCH_3)$, 3: 4.25 mmol of Li_4ebtsa was prepared by the procedure described above. This was suspended into a 10 cm^3 of acetonitrile including a small amount of MeOH with vigorous stirring. A 50 cm^3 of acetonitrile solution including 3.73 g (4.24 mmol) of $(PPh_4)_2[NiCl_4]$ was added to this suspension. This resulted a brown powder in the solution. After the solution had been refluxed for 1.5 h, the powder was removed by filtration. The filtrate and the acetonitrile washings were combined and concentrated to 30 cm^3, to which a 50 cm^3 of acetone was added: the mixture was allowed to stand in a refrigerator for a week. The greenish block crystals which appeared in the flask were collected by decantation and washed with acetonitrile/acetone. Crude yield: 1.20 g (73%). Final purification was done from an acetonitrile/acetone mixed solvent. Found: C, 47.61; H, 5.51; N, 4.40%. Calcd for $C_{24}H_{38}O_8N_2NiS_2$: C, 47.62; H, 6.33; N, 4.63%. The numbers of the solvents were confirmed by ^{1}H NMR. ^{1}H NMR (DMSO-d_6) δ=1.16 (6H, CH_3- of MeOH), 2.10 (12H, -CH_3 of acetone), 3.02 (4H, s, -NCH_2CH_2N-). The ring proton signals of this compound were observed at the same positions as **1**.

$(NEt_4)_2[Ni(H_2tsa)_2](OH)_2$ or $(NEt_4)_2[Ni(Htsa)_2](H_2O)_2$, 5: 1.52 g (0.01 mol) of H_3tsa and 0.4 g (0.01 mol) of NaOH were dissolved in 100 ml of absolute EtOH, to which a solution of $NiCl_2\cdot 6H_2O$ (1.19 g; 0.005 mol)/EtOH(50 cm^3) was added dropwise. The brown precipitates were then filtered off. After solvent had been removed from the filtrate, the residue was mixed with 0.4 g (0.01 mol) of NaOH in 100 cm^3 of water. The resulting wine-red solution was passed through a glass frit. Then the solvent was removed under reduced pressure. The residue was treated with 1.66 g (0.01 mol) of NEt_4Cl in EtOH (50 cm^3) for 20 min. The resulting NaCl was filtered off. The solution was then reduced to 8 cm^3 and mixed with 50 cm^3 of acetone. Stirring for 10 min, and subsequent filtration afforded a polycrystaline brown powder. The crystals were collected, washed with 100 cm^3 of acetone, and dried in vacuo. Yield: 1.14 g. The second crop from the filtrate combined with the washing was 0.74 g. Total yield: 1.88 g (60%). Found: C, 54.57; H, 8.44; N, 8.35%. Calcd for $C_{30}H_{54}N_4NiO_4S_2$, **5**: C, 54.79; H, 8.28; N, 8.52%. ^{1}H NMR (DMSO-d_6) δ=6.56—6.86 (4H, ring), 7.12—7.18 (2H, ring), 7.74—7.84 (2H, ring).

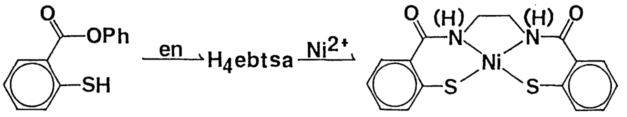
XAFS (EXAFS and XANES) Study: The nickel k-edge X-ray absorptions for $(NEt_4)[Ni(H_2ebtsa)](OH)$, Ni(tsalen), Ni(ebmba), and $(NEt_4)_2[Ni(SPh)_4]$ were measured on the EXAFS facilities at the BL-7C beamline of Photon Factory in the National Laboratory of High Energy Physics (KEK-PF). Syncrotron radiation from the electron storage ring (2.5 GeV, 180—300 mA) was monochromated with a two-crystal Si(111) monochromator. The experiments were carried out at room temperature in transmission mode on polyethylene pellets prepared under an argon atmosphere. Energy calibration was done at the absorption edge of nickel foil (8333eV). The extraction of the EXAFS, $\chi(k)=(\mu(k)-\mu_0(k))/\mu_0(k)$, from the absorption pattern, the Fourier transformation and the curve fitting were processed by using the EXAFS 1 program.[17] The continuous absorption background was subtracted by approximating a Victreen function[18] to the spectrum. The main absorption beyond the edge was smoothed by cubic spline method.

Extracted EXAFS modulation was normalized and then analyzed on the basis of single scattering model.[19]

Other Physicochemical Measurements: The UV-vis. and NIR spectra were recorded on HITACHI 228A and 3400 Spectrophotometers. The electrochemical measurements were performed with a YANACO P-1100 Polarographic Analyzer or a HOKUTO HA-201 Potentiostat/Galvanostat equipped with a FUSO 321 Potential Scanning Unit and a HOKUTO HF-201 Coulomb/Amperehour Meter. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 100 Spectrometer. The IR experiments were carried out with a HITACHI 260-10 Spectrophotometer. Thermogravimetry was performed on a ULVAC TGD 3000M thermal analyzer equipped with a thermal program controller by using a platinum-rhodium cell.

Results and Discussion

Synthesis. In the old method reported by Tanaka, H$_4$ebtsa was prepared from *o*-mercaptobenzoyl chloride.[6,8] In this study we have developed a new route via phenyl *o*-mercaptobenzoate[14] as the precursor. Our method affords crystalline H$_4$ebtsa in a better yield.



The complexation of Li$_4$ebtsa with [NiCl$_4$]$^{2-}$ afforded three kinds of compounds, apparently different in charge. The reaction of Li$_4$ebtsa with (PPh$_4$)$_2$[NiCl$_4$] afforded very deliquescent crystals of (PPh$_4$)[Ni(H$_2$ebtsa)](OH)(H$_2$O), **2**. However, the same reaction system (Li$_4$ebtsa/[NiCl$_4$]$^{2-}$) also led to the formation of highly efflorescent crystals of [Ni(H$_2$ebtsa)]·2(CH$_3$OH)·2(H$_2$O)·2(CH$_3$COCH$_3$), **3**, when the system was conditioned to contain a small amount of MeOH. (NEt$_4$)[Ni(H$_2$ebtsa](OH), **1**, was also obtained from Li$_4$ebtsa and (NEt$_4$)$_2$[NiCl$_4$]. Kruger and Holm reported the isolation of (NEt$_4$)$_2$[Ni(ebtsa)],[8] **4**, from the reaction of H$_4$ebtsa with 4 equiv of NaH and (NEt$_4$)$_2$NiCl$_4$ (the details of the synthesis were not given).

Equality. Table 1 presents the absorption maxima (λ_{max}), the oxidation potentials (E_{ap} or $E_{1/2}$ for Ni^{2+}→Ni^{3+}), and the ^{1}H NMR signals for the chromophores of Compounds **1**—**4**, as well as those for [Ni(ebtsa)]$_2$, **6**.[13] The cyclic voltammograms (CV) for **1**—**3**, as studied with a glassy carbon electrode in DMSO, DMF, or acetonitrile, were all the same, all giving a quasireversible redox couple at $E_{1/2}$=−0.04 V (vs. SCE) for Ni^{3+}/Ni^{2+}. This value is just the same as that reported for **4** by Kruger and Holm.[8]

Table 1. Absorption Maxima and Redox-peak Positions of **1**—**4** and **6**.

Compound	$\lambda_{max}(\varepsilon)$[a]		E_{ap}[b]	E_{cp}[b]
1	585(185)	503(sh, 118)	+0.03[c]	−0.08[c]
2	588(226)	500(sh, 118)	+0.02	−0.08
3	581(178)	500(sh, 130)	+0.01[c]	−0.09[c]
4[8]	581(176)	502(sh, 132)[d]	+0.00[c]	−0.07[c]
6[13]	666(400)	504(450)	+0.40	−1.37

a) nm (10^{-3} mol cm^{2}), observed in DMSO (CH$_3$SOCH$_3$) except for **4**. b) V, vs. SCE. c) In DMF (*N*,*N*-dimethylformamide). d) In EtOH.[8]

1—**3** exhibited two absorption bands, at 581—588 nm (ε 178—200) and at ca. 500 nm (sh, ε 118—130), in DMSO. These bands in the d-d transition region are assigned to any of the three spin-allowed transitions ($^{1}A_{1g}\rightarrow{}^{1}B_{2g}$, $^{1}A_{1g}\rightarrow{}^{1}E_{g}$, and $^{1}A_{1g}\rightarrow{}^{1}B_{1g}$) for a regular, square-planar environment, which are generally not very well-resolved, being obscured by charge-transfer transitions.[20,21] These band features agree well with those of the absorption spectrum of **4** (581 nm (ε 176), 502 nm (sh, 132), in EtOH) reported by Kruger and Holm.[8] A substantial agreement between **1**—**3** was also seen in the ^{1}H NMR of their coordination units. From this conformity, we conclude that Compounds **1**—**4** possess the same coordination unit, at least in solution.

Characterization. The analytical and ^{1}H NMR data for **3** indicate that the coordination unit of **3** is apparently neutral. The data for **1** and **2** show that each of them includes one eq. of NEt$_4$ and PPh$_4$ respectively. Therefore, these compounds are monoanionic from the point of view of apparent charge. On the other hand, the Ni/ebtsa compound reported by Kruger and Holm has a dianionic center, [Ni(ebtsa)]$^{2-}$.[8] All of these compounds seem to have different coordination units in their formal charges, forming a class of compounds describable as [Ni(H$_n$ebtsa)]$^{(2-n)-}$ (n=0, 1, 2). However, as has been mentioned above, they are the same, at least in aprotic solvents. In order to clarify this inconsistency, we undertook several experiments, since this problem is also related to the ionization of the amide protons in aprotic solvents.

The key for understanding this problem is Compound **3**. Because of its apparent neutrality (that is to say, **3** includes no cation in its formula), **3** can be described as Ni(H$_2$ebtsa). On the basis of this, a possible formula for the coordination unit of **1** and **2** seems to be [Ni(H$_2$ebtsa)(OH)]$^{-}$, considering their apparent mono-anionic character. However, the equality of the coordination units of **1**, **2**, and **3** obviates this. **1** and **2** should also have Ni(H$_2$ebtsa), at least in solution. Thus, the OH^{-} anion, which was introduced into the formula of **1** and **2** to explain the elemental analysis, is possibly located in the outer-sphere of the coordination unit, or is eliminated from it in solution.

It is noticed that the analytical data for **1** and **2** can also be interpreted by introducing H$_2$O instead of OH^{-}. If this is true, the ligand can be formulated as Hebtsa^{3-}, in which only one of the two amides is deprotonated, and Compounds **1** and **2** can be described as $(NEt_4)[Ni(Hebtsa)](H_2O)$ and $(PPh_4)[Ni(Hebtsa)](H_2O)_2$ respectivelv.[22] However, it was impossible to observe the release of water from Compound **1** in either the solid phase (thermogravimetry) or in solution (^1H NMR in a strictly dried DMSO-d_6; refluxed three days on CaH_2). The thermogravimetry showed a two-step elimination of one NEt_4OH (one half of the NEt_4OH at 55—100 °C and the remaining half at 100—130 °C). On the other hand, the pH titration using HCl aq. soln. (I=0.2 M NEt_4ClO_4) revealed the monobasic character of **1**, suggesting the existence of a free OH^-. (The compound was decomposed by more than 1.4 equiv of H^+.) Furthermore, the ^{13}C NMRs of **1** and **2** were the same as that of **3** at either the amide carbon (δ 166.9) or the other carbon positions for the coordination unit. Consequently, both **1** and **2** include one equiv of OH^- in the outer sphere of $Ni(H_2ebtsa)$ in solution (DMSO). The inclusion of OH^- in the solid of **1** and **2** upon preparation would be the result of the strong tendency of the amide group to hydrogen-bond, by which means the part anchors OH^- to $Ni(H_2ebtsa)$. In solid **3**, this OH^- would be displaced with the MeOH, H_2O, or acetone.

In contrast with the above-mentioned syntheses, which start from the lithiation of H_4ebtsa, the procedure without an alkaline reagent afforded another ebtsa compound. That is, the reaction of H_4ebtsa with $Ni(acac)_2$ in DMSO gave another bis-complex, $[Ni(H_2ebtsa)]_2$. This was shown by X-ray structural analysis to have two NiS_2O_2 units.[13] Physicochemical properties of **1**—**4** presented in Table 1' are different from those of $[Ni(H_2ebtsa)]_2$. This suggests that the coordination sphere of **1**—**4** is not $\{(S_2O_2\}$ like that of $[Ni(H_2ebtsa)]_2$. It should be $\{S_2N_2\}$.

The Fourier transform of the nickel EXAFS (Fig. 2) for Compound **1** contains, similarly to those for Ni(t-salen) and Ni(ebmba), one major peak which represents a shoulder in the shorter radial region. This major peak was Fourier filtered (FF range; 1.0—2.5 Å) and curve-fitted. The amplitude and the phase function of this peak were fitted to sulfur in the first approximation. The enhancement of the shoulder in the Fourier transformation in a shorter k range (k_{max}<9 Å^{-1}) indicates that the origin of this shoulder is not noise, but light atoms (nitrogen or oxygen). Thus, the major peak was analyzed by a two-atom fit (sulfur and nitrogen or oxygen). The best fit was obtained for $S_{2.1}N(O)_{1.1}$, with the bond distances Ni-S=2.15 Å and Ni-N(O)=1.89 Å. We could not observe any scattering Ni in the second coordination sphere. This suggests a monomeric structure for

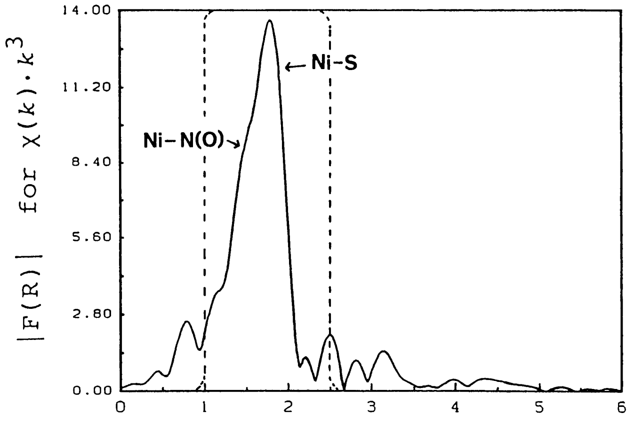


Fig. 2. Fourier transform (k=3.5—10.5 A^{-1}, k^3 weighting) of Ni EXAFS of $(NEt_4)[Ni(H_2ebtsa)](OH)$. The dashed curve represents the filter window used for curve fittings.

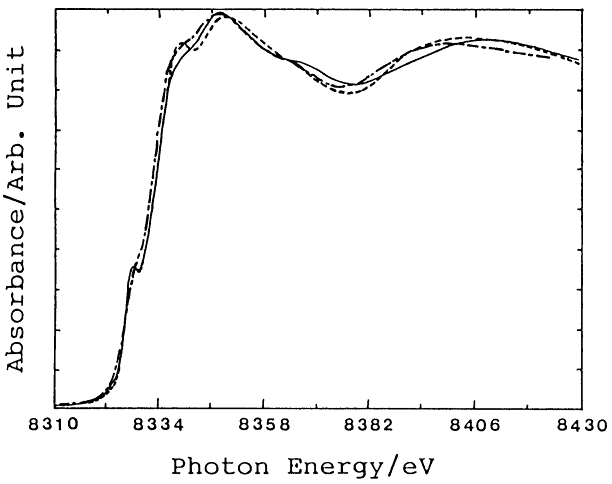


Fig. 3. Normalized Ni K-edge XANES spectra of (a) (NEt_4) $[Ni(H_2ebtsa)](OH)$; (——), (b) Ni(tsalen); (----), and (c) Ni(ebmba); (— - —).

Table 2. Ni-S and Ni-N Bond Distances of $(NEt_4)[Ni(H_2ebtsa)](OH)$, **1**, Ni(tsalen),[a] Ni(ebmba),[b] and $(NEt_4)_2[Ni(SPh)_4]$, as Extracted from the EXAFS Data.

Compounds	Scatterer	EXAFS			X-ray	
		r/Å	N[c]	R[d]	r/Å	N
1	N	1.89	1.1	0.021	—	—
	S	2.15	2.1			
	N[e]	1.89	2.0	0.020		
	S[e]	2.16	2.0			
Ni(tsalen)	N	1.86	1.0	0.044	1.86	2
	S	2.16	1.0		2.15_7	2
	N[e]	1.86	2.0[f]	0.045		
	S[e]	2.16	2.0[f]			
Ni(ebmba)	N	1.94	1.8	0.016	1.94_5	2
	S	2.17	2.5		2.16_7	2
	N[e]	1.96	2.0	0.018		
	S[e]	2.18	2.0			
$[Ni(Sph)_4]^{2-}$	S	2.29	4.1	0.024	2.300	4

a) $H_2tsalen$=N,N'-Ethylenebis(o-mercaptobenzylidenamine. b) H_2ebmba=N,N'-Ethylenebis(o-mercaptobenzylamine. c) Number of scatterers. d) Reliability factor for curve fitting: R= $\{\sum[(\chi\cdot k^3)_{obsd}-(\chi\cdot k^3)_{calc}]^2/\sum[(\chi\cdot k^3)_{obsd}]^2\}^{1/2}$. e) Fixed at 2.

Ni(H_2ebtsa), obviating Ni-S-Ni or Ni-N(O)-Ni bridging. The results are listed in Table 2, together with those for Ni(tsalen), Ni(ebmba), and $[Ni(SPh)_4]^{2-}$.

EXAFS method is not precise in counting the number of back-scatterers. The calculation for light atoms, especially for those interfered by heavy atoms in the Fourier transform, as is seen in Fig. 2, is not reliable. Thus, two ways of curve-fitting were examined (Table 2). In the first calculation, we did not fix the numbers of the back-scatterers. This converged to $NiS_2N(O)$. In the second, we fixed the first coordination sphere as S_2N_2. Practically, there were almost no changes between the two methods in the bond-distance calculations. As a result, **1** is proposed to be four-coordinate, with a $NiS_2N(O)_2$ central unit. The XANES pattern of **1** was almost superimposable on those of Ni(tsalen) and Ni(ebmba), both of which have recently been shown to be S_2N_2 square-planar (Fig. 3).15,16) XANES is now recognized to respond to coordination geometry.23)

Considering all of these findings and the results of UV-vis. and XAFS comparison among **1**—**3** and $[Ni(H_2ebtsa)]_2$, Ni(tsalen), and Ni(ebmba), it can reasonably be concluded that all the compounds, **1**—**3**, have a square-planar $\{S_2N_2\}$ unit.

The amide ligands which have previously been reported are usualy ionized to $-CON^{-}R$ in metal-complexes.24,25) Metal-peptides systems, which provide extensive chemistry for $M-N^{-}$ bonds,24) are examples of this. If our compounds are truely described by Ni(H_2ebtsa), they are the first examples of the complexes which retain N-H bonds in the M-amide part. However, the IR spectra (KBr pellets) of the two metal complexes **1** and **2** did not show any ν_{NH} (and ν_{ND}26)), although the free ligand itself, H_4Ebtsa, showed both ν_{NH} and ν_{ND} (ν_{NH}=3300 cm^{-1}; value of associated secondary amide (broad), ν_{ND}=2470—2400 cm^{-1}; theoretical=2409 cm^{-1} for 3300 cm^{-1}). However, this is not necessarily evidence for the full ionization of the amide protons of Ni(H_2ebtsa) in the solid state, for $(NEt_4)_2[Ni(H_2tsa)_2](OH)_2$ gave no ν_{NH}, either.22) The behavior in the solution was studied by ^{1}H NMR (DMSO-d_4, or DMSO-d_6/CD_3CN=3/1). The amide proton of H_4ebtsa, which was observed at δ 8.51, vanished after the complexation. The amide proton of the Ni-tsa system behaved in the same manner. Furthermore, the ^{13}C NMR for the carbonyl carbon (δ 166.9) of Ni(H_2ebtsa) in DMSO-d_6 did not show any vicinal coupling by the amide proton. However, this was not observed for also the free ligands, probably because of the rapid exchange of amide protons in DMSO-d_6. The possibility of isomerism; -CONH- $\rightleftarrows$ -C(OH)=N- was also obviated by the ^{13}C NMR measurement. Consequently, we could obtain corroborative evidence for neither the presence of a steady N-H bond nor the full ionization of the amide proton of Ni(H_2ebtsa), at least in DMSO. There is still some possibility of the existence of a N-H bond for Ni(H_2ebtsa) in aprotic solvents, considering the similar behavior of the amide proton of $(NEt_4)_2$-$[Ni(H_2tsa)_2](HO)_2$ or $(NEt_4)_2[Ni(Htsa)_2](H_2O)_2$. The denial of the existence of the N-H bond for this complex because of the experimental findings that show no positive evidence for tight N-H binding leads to the erroneous supposition of $-CON^{2-}$ for this complex. This is unlikely.

Oxidation. The peak separation (95 mV) and the i_{pa}/i_{pc} ratio (ca. 1) of CV for **1**—**3** suggest a quasi-reversible character of these complexes for electrode processes. This agrees with the aspects of the chemical oxidation and the reduction of the compounds. Compounds **1**—**3** were easily oxidized to comparably stable species by the I_2 in polar aprotic solvents (DMF, DMSO), changing their colors from dark green (λ_{max}=589 nm) to blue (λ_{max}=720 nm). The oxidized state was gradually quenched to its original state in aprotic solvents, as may be seen in Fig. 4. It was possible to recover almost all of the oxidized species by the further addition of I_2 (dashed line a in Fig. 4). The time course obeys the equation in Fig. 4, which presumes a reaction between the oxidized species and about an equimolar amount of the reductant (experiments revealed that the reductant was not water!) in solutions (DMSO, DMF). The oxidized species of **1**—**3** afforded just the same CV as their reduced form. It was impossible to isolate the oxidized species, which was easily decomposed at a low temperature. The oxidation of **1**—**3** by I_2 in protic solvents (water and

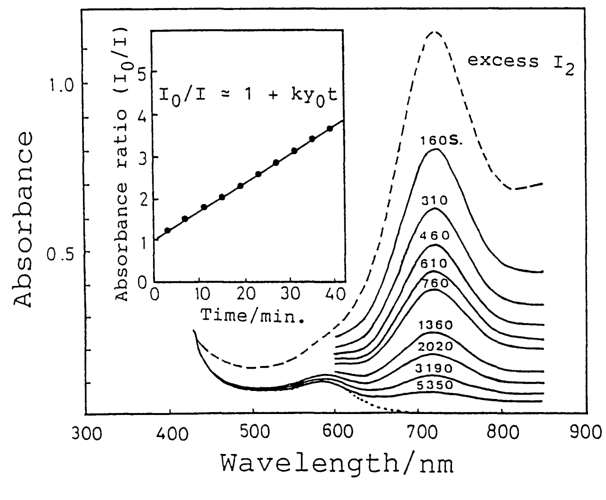


Fig. 4. The time (s) dependent absorption change of oxidized $(NEt_4)[Ni(H_2ebtsa)](OH)$ in DMSO. The dashed line represents the spectrum recovered from the fully quenched one (dotted) by the addition of excess I_2. This time course obeyed the equation;

$$I_0/I \cong 1+ky_0t$$

I; absorbance of the oxidized species at time t.
I_0; the maximum intensity of I that was recovered by the addition of excess (not too much) amount of I_2.
k; reaction rate.
y_0; initial amount of the reductant.
t; time (min).

alcohols) or in aprotic solvents contaminated by water caused the decomposition of the coordination unit.

Ebtsa is not potential as a PAC ligand. It did not ionize the amide proton, nor did stabilize Ni^{3+}. We could not isolate the dianionic unit, $[Ni(ebtsa)]^{2-}$, despite the use of strictly dried solvents in the preparation procedures. In order to overcome the difficulty, it will be necessary to synthesize a new ligand which has electron withdrawing groups on the benezenethiolate rings.

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