

Ni(II) Complexes of *N,N'*-Ethylenebis(*o*-mercaptobenzamide): A Quadridentate Thiolato Amide {S₂N₂} Ligand

Takeshi YAMAMURA,* Makoto TADOKORO, Nobuhumi NAKAMURA, Koji TANAKA, and Kiyotaka ASAKURA†
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162

†Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
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Three nickel(II) complexes with *N,N'*-ethylenebis(*o*-mercaptobenzamide), H₄ebtsa, a quadridentate {S₂N₂} 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(H₂ebtsa). EXAFS and XANES study was undertaken for one of the new compounds, and the results were compared with those for similar three NiS₂N₂ complexes, (*N,N'*-ethylenebis(*o*-mercaptobenzylidenaminato))Ni(II), (*N,N'*-ethylenebis(*o*-mercaptobenzylaminato))Ni(II) and (NEt₄)[Ni-(SPh)₄]. From these results and a comparison with the results for [Ni(ebtsa)]₂, it was concluded that a square planar {S₂N₂} unit was reliable as the coordination sphere of Ni(H₂ebtsa). 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⁾ H₄ebtsa (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 (Cu³⁺),²⁾ and cobalt (Co⁴⁺).³⁾

Recently, Cruger and Holm⁸⁾ have reported the synthesis of (NEt₄)₂[Ni(ebtsa)] and shown the trap of Ni³⁺ in an electrolytic EPR cell. We ourselves also have previously reported, independently, the synthesis of (NEt₄)[Ni(H₂ebtsa)](OH) and the generation of Ni³⁺ 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 Ni³⁺ sites of uptake hydrogenases,^{10–12)} which oxidize H₂. 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_nebtsa)]^{(2–n)–} [*n*=0, 1, 2] on the basis of the analytical and ¹H NMR data, the comparative studies of these compounds with Ni(tsalen),*** Ni(ebmbsa),*** and [Ni(H₂ebtsa)]₂¹³⁾ by using UV-vis. and XAFS (XANES and EXAFS) measurements have revealed that they have the same coordination unit, Ni(H₂ebtsa), with a square planar NiS₂N₂ coordination sphere. Their IR (in solid) and NMR (in solution) signals were compared with those of (NEt₄)₂[Ni(H₂tsa)](OH)₂,*** in order to reveal the ionization character of the amide hydrogen of Ni(H₂ebtsa). It was impossible to obtain evidence for a steady N–H bond in the coordination unit.

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(ebmbsa) were prepared by the published methods.^{15,16)}

H₄ebtsa: 25.9 g (0.113 mol) of thiosalol was dissolved in 250 cm³ 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 cm³ portions of xylene, and dried in vacuo. This material was washed further with three 100 cm³ portions of hot EtOH. The residue was then treated with 100 cm³ of EtOH at room temperature, and the white suspension observed in the solution was removed by

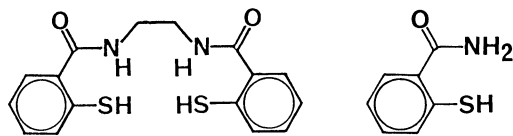


Fig. 1. Right; H₄ebtsa=*N,N'*-ethylenebis(*o*-mercaptobenzamide) or *N,N'*-ethylenebis(thiosalicylamide).

Left; H₃tsa=*o*-mercaptobenzamide or thiosalicylamide.

** H₄ebtsa=*N,N'*-ethylenebis(*o*-mercaptobenzamide) or *N,N'*-ethylenebis(thiosalicylamide).

*** H₃tsa=*o*-mercaptobenzamide or thiosalicylamide.
H₂tsalen=*N,N'*-ethylenebis(*o*-mercaptobenzylidenamine) or *N,N'*-ethylenebis(thiosalicylidenamine).¹⁵⁾
H₂ebmba=*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 cm³ 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 C₁₆H₁₆O₂N₂S₂: C, 57.81; H, 4.85; N, 8.43%. ¹H 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, -NCH₂CH₂N-).

H₃tsa: 18 g (78.2 mmol) of thiosalol was dissolved in 300 cm³ 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 C₇H₇NOS: C, 54.88; H, 4.61; N, 9.14; S, 20.93%. ¹H NMR (DMSO-*d*₆) δ=8.00 (2H, d, -CONH₂), 7.69–7.08 (4H, 4H), 5.43 (1H, s, -SH).

(NEt₄)[Ni(H₂ebtsa)](OH), 1: 3.06 mmol of Li₄ebtsa was prepared by dissolving 0.085 g (12.2 mmol) of lithium metal and 1.02 g (3.06 mmol) of H₄ebtsa in MeOH. The MeOH was then removed completely. The Li₄ebtsa was suspended in 10 cm³ of acetonitrile, to which a 50 cm³ of acetonitrile solution containing 1.9 g of (NEt₄)₂NiBr₄ 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 cm³ 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 C₂₄H₃₅N₃O₃S₂Ni: C, 53.74; H, 6.58; N, 7.83%. ¹H NMR (DMSO-*d*₆) δ=1.04–1.22 (12H, t, cation's -CH₃), 3.00 (4H, s, -NCH₂CH₂N-), 3.09–3.30 (8H, q, cation's -CH₂), 6.53–6.79 (4H, ring proton), 7.00–7.09 (2H, ring proton), 7.81–7.90 (2H, ring proton).

(PPh₄)[Ni(H₂ebtsa)](OH)(H₂O), 2: 6.02 mmol of Li₄ebtsa was prepared from 2.00 g (6.02 mmol) of H₄ebtsa and 0.17 g (24.1 mmol) of lithium in 60 cm³ of MeOH. After the solvent had been removed, and the residue dried well under a vacuum, 40 cm³ of acetonitrile was introduced into the flask, into which an acetonitrile solution (50 cm³) containing 5.29 g (6.02 mmol) of (PPh₄)₂[NiCl₄] 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 cm³ of acetonitrile, and the brown precipitates which appeared again in the solution were filtered off. The filtrate was mixed with a 75 cm³ of acetone, and left at -10°C for 2 days. The fine powders which then appeared in the solution were filtered 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 C₄₀H₃₇O₄N₂NiPS₂: C, 62.92; H, 4.88; N, 3.67%. ¹H NMR (DMSO-*d*₆) δ=3.02 (4H, s, -NCH₂CH₂N-), 6.41–6.79,

6.84–7.12 (6H, ring proton/ligand), 7.48–8.24 (22H, ring proton/ligand and cation).

[Ni(H₂ebtsa)]₂(CH₃OH)₂(H₂O)₂(CH₃COCH₃), 3: 4.25 mmol of Li₄ebtsa was prepared by the procedure described above. This was suspended into a 10 cm³ of acetonitrile including a small amount of MeOH with vigorous stirring. A 50 cm³ of acetonitrile solution including 3.73 g (4.24 mmol) of (PPh₄)₂[NiCl₄] 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 cm³, to which a 50 cm³ 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 C₂₄H₃₈O₈N₂NiS₂: C, 47.62; H, 6.33; N, 4.63%. The numbers of the solvents were confirmed by ¹H NMR. ¹H NMR (DMSO-*d*₆) δ=1.16 (6H, CH₃- of MeOH), 2.10 (12H, -CH₃ of acetone), 3.02 (4H, s, -NCH₂CH₂N-). The ring proton signals of this compound were observed at the same positions as 1.

(NEt₄)₂[Ni(H₂tsa)₂](OH)₂ or (NEt₄)₂[Ni(Htsa)₂](H₂O)₂, 5: 1.52 g (0.01 mol) of H₃tsa and 0.4 g (0.01 mol) of NaOH were dissolved in 100 ml of absolute EtOH, to which a solution of NiCl₂·6H₂O (1.19 g; 0.005 mol)/EtOH(50 cm³) 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 cm³ 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 NEt₄Cl in EtOH (50 cm³) for 20 min. The resulting NaCl was filtered off. The solution was then reduced to 8 cm³ and mixed with 50 cm³ of acetone. Stirring for 10 min, and subsequent filtration afforded a polycrystalline brown powder. The crystals were collected, washed with 100 cm³ 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 C₃₀H₅₄N₄NiO₄S₂, 5: C, 54.79; H, 8.28; N, 8.52%. ¹H 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 (NEt₄)[Ni(H₂ebtsa)](OH), Ni(tsalen), Ni(ebmbsa), and (NEt₄)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). Synchrotron 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 function¹⁸⁾ to the spectrum. The main absorption beyond the edge was smoothed by cubic spline method.

It is noticed that the analytical data for **1** and **2** can also be interpreted by introducing H₂O instead of OH⁻. If this is true, the ligand can be formulated as Hebtsa³⁻, in which only one of the two amides is deprotonated, and Compounds **1** and **2** can

be described as $(\text{NEt}_4)[\text{Ni}(\text{Hebtsa})](\text{H}_2\text{O})$ and $(\text{PPh}_4)[\text{Ni}(\text{Hebtsa})](\text{H}_2\text{O})_2$ respectively.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 $\text{DMSO}-d_6$; refluxed three days on CaH_2). The thermogravimetry showed a two-step elimination of one NEt_4OH (one half of the NEt_4OH at $55\text{--}100^\circ\text{C}$ and the remaining half at $100\text{--}130^\circ\text{C}$). On the other hand, the pH titration using HCl aq. soln. ($I=0.2\text{ M}$ 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 $\text{Ni}(\text{H}_2\text{ebtsa})$ 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 $\text{Ni}(\text{H}_2\text{ebtsa})$. 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 $\text{Ni}(\text{acac})_2$ in DMSO gave another bis-complex, $[\text{Ni}(\text{H}_2\text{ebtsa})]_2$. 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 $[\text{Ni}(\text{H}_2\text{ebtsa})]_2$. This suggests that the coordination sphere of **1**—**4** is not $\{\text{S}_2\text{O}_2\}$ like that of $[\text{Ni}(\text{H}_2\text{ebtsa})]_2$. It should be $\{\text{S}_2\text{N}_2\}$.

The Fourier transform of the nickel EXAFS (Fig. 2) for Compound **1** contains, similarly to those for $\text{Ni}(\text{tsalen})$ and $\text{Ni}(\text{ebmba})$, one major peak which represents

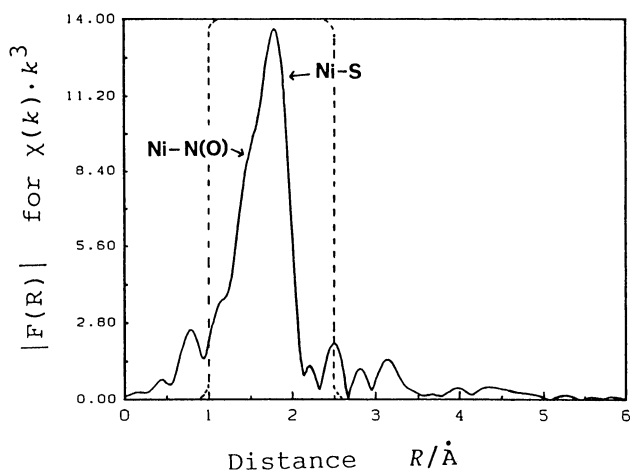


Fig. 2. Fourier transform ($k=3.5\text{--}10.5\text{ Å}^{-1}$, k^3 weighting) of Ni EXAFS of $(\text{NEt}_4)[\text{Ni}(\text{H}_2\text{ebtsa})](\text{OH})$. The dashed curve represents the filter window used for curve fittings.

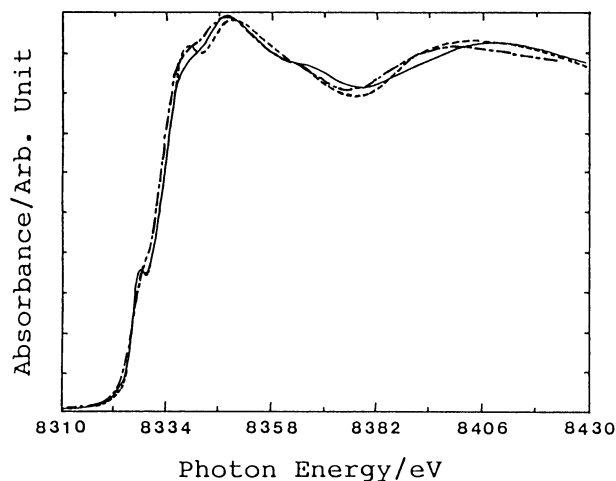


Fig. 3. Normalized Ni K-edge XANES spectra of (a) $(\text{NEt}_4)[\text{Ni}(\text{H}_2\text{ebtsa})](\text{OH})$; (—), (b) $\text{Ni}(\text{tsalen})$; (----), and (c) $\text{Ni}(\text{ebmba})$; (- - -).

ents a shoulder in the shorter radial region. This major peak was Fourier filtered (FF range; $1.0\text{--}2.5\text{ Å}$) 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 ($k_{\text{max}} < 9\text{ Å}^{-1}$) 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 $\text{S}_{2.1}\text{N}(\text{O})_{1.1}$, with the bond distances $\text{Ni-S}=2.15\text{ Å}$ and $\text{Ni-N}(\text{O})=1.89\text{ Å}$. We could not observe any scattering Ni in the second coordination sphere. This suggests a monomeric structure for

Table 2. Ni-S and Ni-N Bond Distances of $(\text{NEt}_4)[\text{Ni}(\text{H}_2\text{ebtsa})](\text{OH})$, **1**, $\text{Ni}(\text{tsalen})$,^{a)} $\text{Ni}(\text{ebmba})$,^{b)} and $(\text{NEt}_4)_2[\text{Ni}(\text{SPh})_4]$, as Extracted from the EXAFS Data.

Compounds	Scatterer	EXAFS			X-ray	
		$r/\text{Å}$	N^c	R^d	$r/\text{Å}$	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			
$\text{Ni}(\text{tsalen})$	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)}			
$\text{Ni}(\text{ebmba})$	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			
$[\text{Ni}(\text{Sph})_4]^{2-}$	S	2.29	4.1	0.024	2.300	4

a) $\text{H}_2\text{tsalen}=\text{N},\text{N}'\text{-Ethylenebis}(o\text{-mercaptobenzylidenamine})$. b) $\text{H}_2\text{ebmba}=\text{N},\text{N}'\text{-Ethylenebis}(o\text{-mercaptobenzylamine})$. c) Number of scatterers. d) Reliability factor for curve fitting: $R=\{\sum[(\chi \cdot k^3)_{\text{obsd}}-(\chi \cdot k^3)_{\text{calc}}]^2/\sum[(\chi \cdot k^3)_{\text{obsd}}]^2\}^{1/2}$. e) Fixed at 2.

Ni(H₂ebtsa), obviating Ni-S-Ni or Ni-N(O)-Ni bridging. The results are listed in Table 2, together with those for Ni(tsalen), Ni(ebmbsa), 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 NiS₂N(O). In the second, we fixed the first coordination sphere as S₂N₂. 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 NiS₂N(O)₂ central unit. The XANES pattern of **1** was almost superimposable on those of Ni(tsalen) and Ni(ebmbsa), both of which have recently been shown to be S₂N₂ 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(H₂ebtsa)₂], Ni(tsalen), and Ni(ebmbsa), it can reasonably be concluded that all the compounds, **1**–**3**, have a square-planar {S₂N₂} unit.

The amide ligands which have previously been reported are usually 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 truly described by Ni(H₂ebtsa), 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, H₄ebtsa, 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(H₂ebtsa) in the solid state, for (NEt₄)₂[Ni(H₂tsa)₂](OH)₂ gave no ν_{NH} , either.²²⁾ The behavior in the solution was studied by ¹H NMR (DMSO-*d*₆, or DMSO-*d*₆/CD₃CN=3/1). The amide proton of H₄ebtsa, 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 ¹³C NMR for the carbonyl carbon (δ 166.9) of Ni(H₂ebtsa) 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– $\rightleftharpoons$ –C(OH)=N– was also obviated by the ¹³C 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(H₂ebtsa), at least in DMSO. There is still some possibility of the existence of a N–H bond for

Ni(H₂ebtsa) in aprotic solvents, considering the similar behavior of the amide proton of (NEt₄)₂–[Ni(H₂tsa)₂](HO)₂ or (NEt₄)₂[Ni(Htsa)₂](H₂O)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 $i_{\text{pa}}/i_{\text{pc}}$ 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 I₂ 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 I₂ (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 I₂ in protic solvents (water and

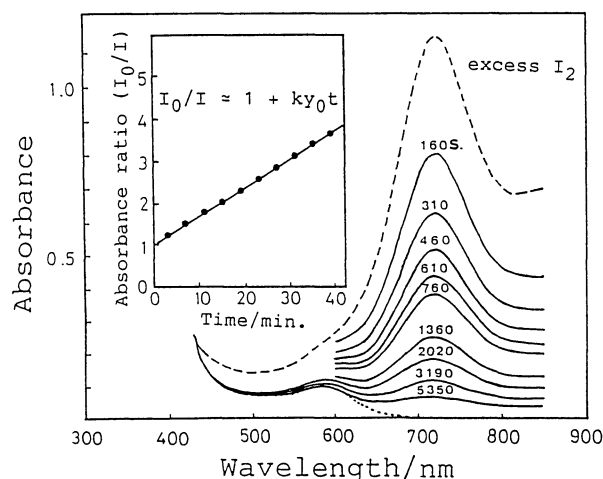


Fig. 4. The time (s) dependent absorption change of oxidized (NEt₄)[Ni(H₂ebtsa)](OH) in DMSO. The dashed line represents the spectrum recovered from the fully quenched one (dotted) by the addition of excess I₂. This time course obeyed the equation;

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

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 I₂.

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, $[\text{Ni}(\text{ebtsa})]^{2-}$, 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 benzenethiolate rings.

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