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Communication

Novel Thiosalamo Ligand as a Remarkably Stable N_2S_2 Salen-Type Chelate and Synthesis of a Nickel(II) Complex

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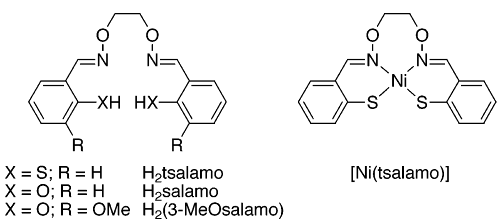
Novel N_2S_2 tetradentate chelate ligand H_2tsalamo, which contains both thiol groups and C═N moieties, was synthesized as a remarkably stable compound. Complexation between H_2tsalamo and nickel(II) acetate gave a square planar complex [Ni(tsalamo)] as dark brown crystals, whose structure was determined by X-ray crystallography. In contrast, the corresponding N_2O_2 ligands, salamo and 3-MeOsalamo, gave trinuclear and mononuclear complexes, respectively, in which all the nickel atoms have octahedral geometry.

Nickel(II) complexes of a chelate ligand containing sulfur and nitrogen donors have recently attracted much attention because they are used as a model for the nickel center of enzymes such as bifunctional carbon monoxide dehydrogenase/acetyl-CoA synthase and nickel-containing superoxide dismutase.[1] Thus, *N*,*N*′-bis(thiosalicylidene)ethylenediamine (═H_2tsalen) would be a suitable candidate because high coordination ability similar to that of the oxygen analogue, H_2salen,[2] is expected. Furthermore, N_2S_2 ligands containing thiolato groups are useful as a building block for heteromultinuclear clusters.[1c,3] However, H_2tsalen is too unstable to be isolated because it readily undergoes cyclization to give a bicyclo[3.3.1]nonane derivative.[4,5] On the other hand, their metal complexes have been synthesized and characterized, although the free ligands were not isolated.[4,6−10] We have recently reported that H_2salamo (═1,2-bis(salicylideneaminooxy)ethane), an oxime analogue of H_2salen, is sufficiently stable to resist scrambling of the C═N bonds.[11] This may be ascribed to the lower reactivity of the oxime C═N bonds toward nucleophiles.

Consequently, 1,2-bis(thiosalicylideneaminooxy)ethane (═H_2tsalamo), is expected to be much more stable than its imine analogue H_2tsalen. In this communication, we report the first isolation of a salen-type chelate ligand containing a thiosalicylidene moiety and the synthesis of its nickel(II) complex.



The synthesis of H_2tsalamo is shown in Scheme 1. The reaction of the thiosalicylaldehyde[5b,12,13] with 1,2-bis(aminooxy)ethane[14] afforded the H_2tsalamo in 47% yield as colorless crystals.[15] H_2tsalamo is remarkably stable both in the solid state and in solution. The ^{1}H NMR spectrum of H_2tsalamo in $CDCl_3$ was not changed even after several days.[15] Thus,

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(12) Thiosalicylaldehyde cannot be isolated because the compound partly decomposes upon removing the solvent.[13] For this reason, the compound was kept in solution and used for the next reaction without isolation.

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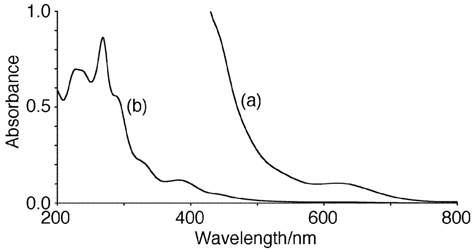
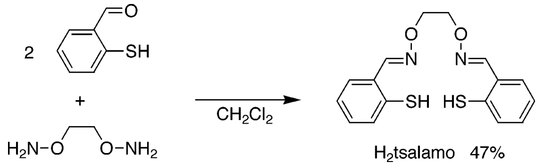


Figure 1. Absorption spectra of [Ni(tsalamo)] in acetonitrile at (a) 0.4 mM and (b) 0.02 mM.

Scheme 1. Synthesis of H_2tsalamo



the oxime ligand H_2tsalamo is much more stable than H_2-tsalen. However, H_2tsalamo in highly diluted solution decomposed very slowly under aerobic conditions probably due to autoxidation. Thus, H_2tsalamo is less stable than H_2-salamo.

H_2tsalamo reacted with nickel(II) acetate in dichloromethane/methanol to afford the corresponding nickel(II) complex as dark brown crystals in 67% yield. Elemental analysis is consistent with the formula of the mononuclear complex [Ni(tsalamo)].[16] A peak at $m/z = 387.98$ [Ni(tsalamo)]$^+$ in the ESI-mass spectrum (Figures S1 and S2, Supporting Information) also supports the mononuclear structure. Furthermore, in the ^{1}H NMR spectrum of the nickel(II) complex in $CDCl_3$ six sharp signals appeared, indicating the exclusive formation of a symmetrical and diamagnetic complex. In the electronic absorption spectra, d−d transition was observed at 620 nm ($\epsilon = 260$) and an LMCT band was observed at 382 nm ($\epsilon = 6000$) (Figure 1), which are characteristic of low-spin square planar nickel(II) complexes with N_2S_2 coordination spheres.[17] This simple and easy preparation of the metal complex with an N_2S_2 chelate contrasts with the laborious synthesis using the corresponding imine analogue H_2tsalen.[4,6−10]

X-ray crystallographic analysis revealed the structure of the nickel(II) complex (Figure 2).[18] The four atoms of the donor set (N1, N2, S1, S2) and Ni1 essentially lie in a plane. The dihedral angle between the two coordination planes, N1−Ni1−S1 and N2−Ni1−S2, is 7.96(9)°, indicating slight distortion toward tetrahedral geometry from the square planar structure. It is noteworthy that the coordination bonds of one thiosalicylidene moiety (Ni1−S2, 2.1973(7) Å; Ni1−N2, 1.9462(19) Å) are considerably longer than those of the other (Ni1−S1, 2.1399(6) Å; Ni1−N1, 1.897(2) Å) (Table 1). The differences (0.057 Å for Ni−S and 0.049 Å for Ni−N) are much larger than those of the known nickel(II) complexes of thiosalicylidenediamine N_2S_2 ligands (less than 0.035 Å for Ni−S and 0.014 Å for Ni−N).[9,10,19−22]

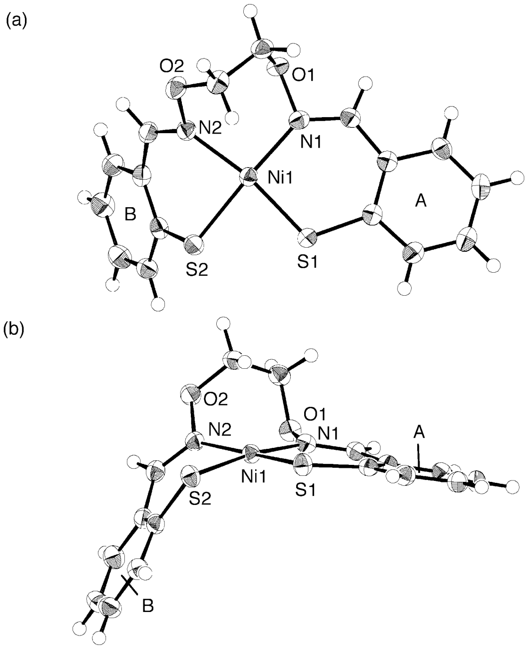
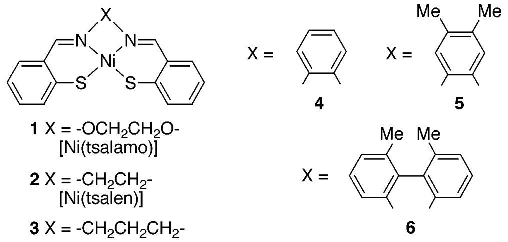


Figure 2. Crystal structure of [Ni(tsalamo)] (50% probability level): (a) top view and (b) side view.

Table 1. Ni−S and Ni−N Bond Lengths of Tsalen-Type N_2S_2 Chelate Complex of Nickel(II)



1 X = $-OCH_2CH_2O-$
[Ni(tsalamo)]
2 X = $-CH_2CH_2-$
[Ni(tsalen)]
3 X = $-CH_2CH_2CH_2-$

complex	Ni−S1	Ni−S2	Ni−N1	Ni−N2
1[a]	2.1399(6)	2.1973(7)	1.897(2)	1.9462(19)
2[b]	2.139(5)	2.174(5)	1.85(1)	1.86(1)
2[c] (A[d])	2.145(2)	2.155(2)	1.883(4)	1.876(4)
2[c] (B[d])	2.150(2)	2.155(2)	1.885(5)	1.891(5)
3[e] (A[d])	2.1454(8)	2.1733(8)	1.916(2)	1.909(2)
3[e] (B[d])	2.1610(9)	2.1686(9)	1.919(2)	1.913(2)
4[f]	2.1519(6)	2.1587(6)	1.8992(17)	1.9014(15)
5[g]	2.174(1)		1.920(3)	
6[h]	2.152(2)	2.184(2)	1.931(5)	1.917(6)

[a] This work. [b] Reference 9. [c] Reference 10. [d] A and B denote two crystallographically independent molecules. [e] Reference 19. [f] Reference 20. [g] Reference 21. [h] Reference 22.

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(15) Data for H_2tsalamo: colorless crystals, mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 4H), 4.61 (s, 2H), 7.16 (td, $J = 7.4$, 1.5 Hz, 2H), 7.20 (td, $J = 7.4$, 1.5 Hz, 2H), 7.32 (dd, $J = 7.4$, 1.5 Hz, 2H), 7.52 (dd, $J = 7.4$, 1.5 Hz, 2H), 8.42 (s, 2H). Anal. Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43. Found: C, 57.67; H, 4.74; N, 7.72.

(16) Data for [Ni(tsalamo)]: dark brown crystals; ^{1}H NMR ($CDCl_3$) δ 4.85 (s, 4H), 7.06 (td, $J = 7.8$, 1.2 Hz, 2H), 7.17 (td, $J = 7.8$, 1.2 Hz, 2H), 7.22 (dd, $J = 7.8$, 1.2 Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 8.16 (s, 2H). Anal. Calcd for $C_{16}H_{14}N_2NiO_2S_2$: C, 49.39; H, 3.63; N, 7.20. Found: C, 49.83; H, 3.94; N, 6.98.

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(18) Crystallographic data for [Ni(tsalamo)]: $C_{16}H_{14}N_2NiO_2S_2$ (389.12), monoclinic, $P2_1/a$, $a = 8.0198(7)$ Å, $b = 19.6504(14)$ Å, $c = 9.8681(7)$ Å, $\beta = 94.882(3)°$, $V = 1549.5(2)$ Å^3, $Z = 4$, $T = 150$ K, $D_{calcd} = 1.668$ g cm^{-3}, μ(Mo Kα) = 1.531 mm^{-1}, $R1 = 0.0443$ ($I > 2\sigma(I)$), $wR2 = 0.1136$ (all data).[26]

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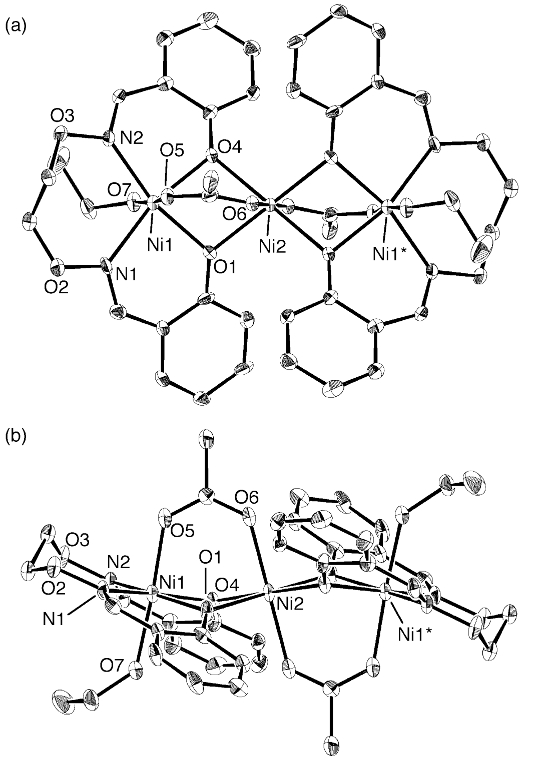

Figure 3. Crystal structure of $[Ni_3(salamo)_2(OAc)_2(EtOH)_2]$ (ORTEP, 50% probability level). One of the crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity: (a) top view and (b) side view.

The dihedral angle between the coordination plane (defined as the least-squares plane of Ni1, N1, N2, S1, and S2) and the benzene ring B (56.7°) is considerably larger than that for the benzene ring A (14.6°). Thus, the molecule is bent at the S2−N2 line. The elongation of the coordination bonds, Ni1−S2 and Ni1−N2, indicates weaker interaction of the ligand with the nickel center,[22] probably due to the distorted geometry of the complex.

In contrast to the complexation of H_2tsalamo with nickel(II) acetate, the reaction of the oxygen analogue, H_2salamo, with nickel(II) acetate gave a trinuclear complex $[Ni_3(salamo)_2(OAc)_2(EtOH)_2]$ (Figure 3).[23,24] All the nickel atoms of the complex have an octahedral geometry. A similar trinuclear complex was obtained from zinc(II) acetate and H_2salamo, although no ethanol molecules coordinate to the metals bound in the ligand.[11b]

Interestingly, binding behavior of the methoxy analogue H_2(3-MeOsalamo) toward nickel(II) is strikingly different from that of H_2salamo to give a mononuclear complex $[Ni(3\text{-}MeOsalamo)(H_2O)_2]$ upon the complexation (Figure 4).[25] The nickel atom has an octahedral geometry possessing water molecules at the two axial sites. Noteworthy is that complexation of H_2(3-MeOsalamo) with zinc(II) acetate afforded the corresponding trinuclear complex.[11b]

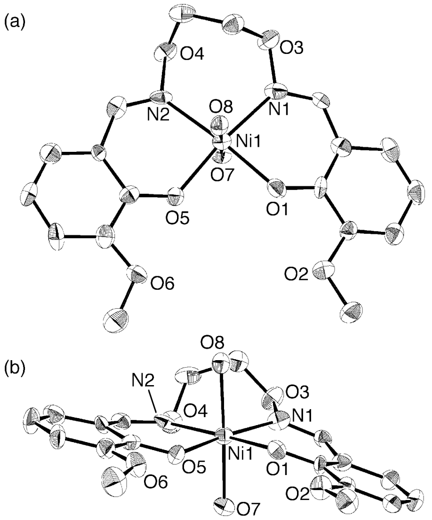

Figure 4. Crystal structure of $[Ni(3\text{-}MeOsalamo)(H_2O)_2]$ (30% probability level). Hydrogen atoms are omitted for clarity: (a) top view and (b) side view.

In conclusion, we have synthesized and isolated a new oxime-type N_2S_2 ligand, H_2tsalamo, which is much more stable than the imine analogue, H_2tsalen. The tsalamo gave the mononuclear nickel(II) complex [Ni(tsalamo)] as seen in the imine analogues. The tsalamo unit would be a useful building block for metallo-supramolecules to incorporate an N_2S_2 chelate site. Further investigation on the tsalamo-complexes of other transition metals such as manganese, cobalt, iron, etc. is now in progress.

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Supporting Information Available: Crystallographic data for [Ni(tsalamo)], $[Ni_3(salamo)_2(OAc)_2(EtOH)_2]$, and $[Ni(3\text{-}MeOsalamo)(H_2O)_2]$ in CIF formats and ESI mass spectrum of [Ni(tsalamo)] in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Crystallographic data for $[Ni_3(salamo)_2(OAc)_2(EtOH)_2]$: $C_{42}H_{52}N_4Ni_3O_{15}$ (1029.01), triclinic, $P\bar{1}$, $a = 10.7606(17)$ Å, $b = 12.4817(18)$ Å, $c = 16.8606(19)$ Å, $\alpha = 89.042(6)°$, $\beta = 83.680(6)°$, $\gamma = 78.832(3)°$, $V = 2208.1(5)$ Å^3, $Z = 2$, $T = 120$ K, $D_{calcd} = 1.548$ g cm^{-3}, μ(Mo Kα) = 1.340 mm^{-1}, $R1 = 0.0551$ ($I > 2\sigma(I)$), $wR2 = 0.1335$ (all data).[26]

(25) Crystallographic data for $[Ni(3\text{-}MeOsalamo)(H_2O)_2]$: $C_{18}H_{22}N_2NiO_8$ (453.09), monoclinic, *Cc*, $a = 23.795(4)$ Å, $b = 10.8068(16)$ Å, $c = 7.5256(15)$ Å, $\beta = 107.184(10)°$, $V = 1848.8(6)$ Å^3, $Z = 4$, $T = 296$ K, $D_{calcd} = 1.628$ g cm^{-3}, μ(Mo Kα) = 1.101 mm^{-1}, $R1 = 0.0741$ ($I > 2\sigma(I)$), $wR2 = 0.2095$ (all data).[26]

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