

[Bis{ μ -N,N'-bis(*o*-thiobenzoyl)ethylenediamine-S,O,O',S'}-dinickel(II)].
 Synthesis of a $2 \times \{S_2O_2\}$ Bis-complex and the Structural Analysis

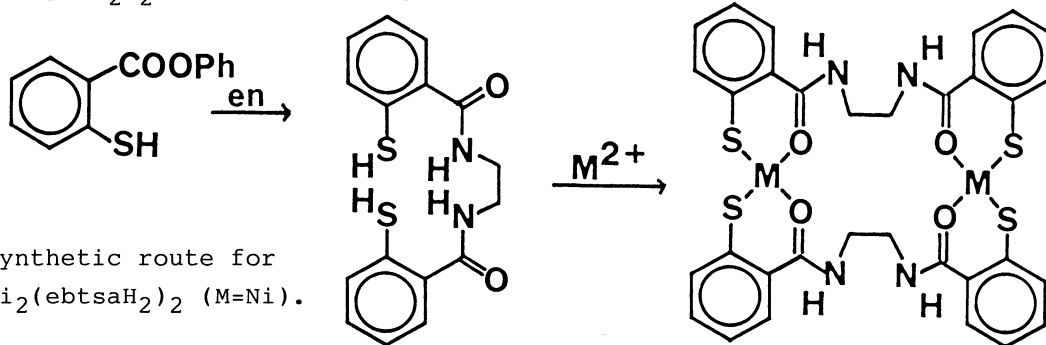
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N,N'-Bis(*o*-thiobenzoyl)ethylenediamine reacted with Ni^{2+} in acetone to form a bis-complex, in which two square planar NiS_2O_2 units are connected with each other by two ethylene bridges.

In the previous papers we have reported the syntheses and the structures of two types of NiS_2N_2 square planar complexes; (N,N'-ethylenebis(thiosalicylidene-aminato)nickel(II), **1**, $Ni(tsalen)$,¹⁾ and (N,N'-ethylenebis(*o*-mercaptobenzyl-aminato)nickel(II), **2**, $Ni(ebmbsa)$.²⁾ N,N'-Bis(*o*-thiobenzoyl)ethylenediamine, or N,N'-ethylenebis(thiosalicylamide), **ebtsaH**₄³⁾ (Scheme 1) also belongs to a potential $\{S_2N_2\}$ ligand, which has recently been shown to form a nickel complex, $(NEt_4)_2[Ni(ebtsa)]$, **3**, by H. J. Crüger and R. H. Holm⁴⁾ without the structural evidence for NiS_2N_2 coordination. In this short paper we represent that the same ligand affords a different novel bis-complex in which each of the two nickel ions is surrounded by $\{S_2O_2\}$ coordination sphere.



Scheme 1. Synthetic route for
 $Ni_2(ebtsaH_2)_2$ ($M=Ni$).

EbtsaH₄ was prepared by treating thiosarole⁵⁾ with ethylenediamine in xylene, differently from the old method.^{3,6)} Crystals of the title biscomplex, $Ni_2(ebtsa)_2 \cdot 2(CH_3COCH_3)$, **4**, grew up in triclinic form in the reaction mixture of the free ligand and $Ni(acac)_2 \cdot 2H_2O$ in acetone (Scheme 1). The crystal parameters and the experimental condition are as follows: $a=9.363(2)$ Å, $b=14.279(2)$ Å, $c=8.201(2)$ Å, $\alpha=93.58(2)$ deg., $\beta=115.37(1)$ deg., $\gamma=96.30(2)$ deg., $V=977.4(3)$ Å³. Space group P1, $Z=2$, $D_{calc}=1.52$ g cm⁻³. RIGAKU AFC5R, Mo-K α ($\lambda=0.71069$ Å, graphite monochromated), $\mu(Mo-K\alpha)=12.19$ cm⁻¹, No. of observations ($I>3.00(\sigma(I))$)=2553 $R=0.042$.

The molecule (Fig. 2) is centrosymmetric, consists of two square planar units

which are staggered with each other. Each metal center is surrounded by *cis*-symmetric two sulfur atoms of thiophenolates and two carbonyl oxygen atoms of the amides. The dislocations of the component atoms from the least squares plane for NiS_2O_2 are as follows: Ni; $-0.0030(4)$ Å, S_1 ; $0.0357(10)$ Å, S_2 ; $-0.0501(12)$ Å, O_1 ; $-0.2069(22)$ Å, O_2 ; $0.2493(24)$ Å. Thus, NiS_2O_2 is tetrahedrally distorted. The benzene rings are not coplanar, bent from this least squares plane with dihedral angles 20.40° and 29.00° , probably tensioned by the ethylene bridges, which also causes the staggered situation between the two NiS_2O_2 units mentioned above.

Ni-S ₁	2.125(1)
Ni-S ₂	2.126(1)
Ni-O ₁	1.877(3)
Ni-O ₂	1.889(3)
C ₁₇ -O ₁	1.266(4)
C ₂₇ -O ₂	1.253(5)
S ₁ -Ni-S ₂	86.10(5)
S ₂ -Ni-O ₂	94.0(1)
O ₂ -Ni-O ₁	85.6(1)
S ₁ -Ni-O ₁	95.41(9)

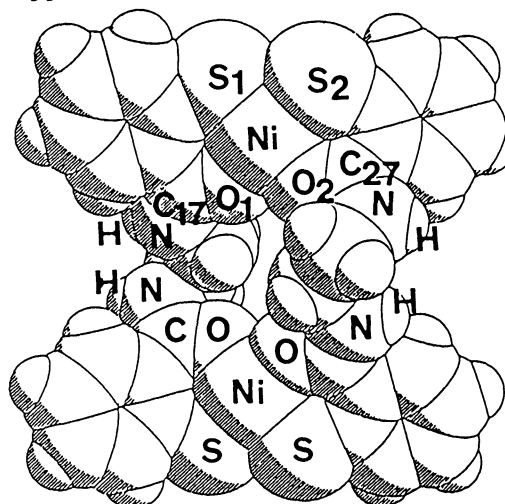


Fig. 2. A van der Waals drawing of Bis [$\{\mu\text{-N,N'}$ -bis(*o*-thiobenzoyl)ethylenediamine- $\text{S},\text{O},\text{O}',\text{S}'$ }-]dinickel(II)]. Selected bond lengths (Å) and angles (deg.).

$[\text{Ni}(\text{ebtsa})]^{2-}$ in reference 4) involves the ligand in a tetra anionic form, hence in a thiolato amidato form if it is true (No analytical and structural data were presented in the literature). The amide protons of ebtsaH_4 are, as well as thiophenolate protons, ionized easily to form ebtsa^{4-} , thus under basic condition, it would certainly works as a PAC (polyanionic chelating) ligand for Ni^{2+} also as the salicylamidato analogs did for cobalt and copper, stabilizing the high oxidation states, Co^{4+} , 7) and Cu^{3+} , 8) On the contrally to this, our complex still contains amide protons (Fig. 2, ^1H NMR in $\text{DMSO}-d_6$). The ligand is described ebtsaH_2^{2-} , eventually. The new compound provides a novel example for a bis-complex including CO-metal ion bonds, as well as thiolato-metal ion bonds.

References

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