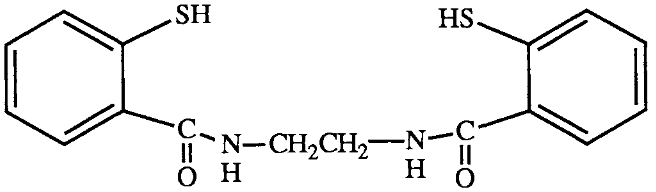
CHEMISTRY LETTERS, pp. 983-986, 1990.

The Structure of a Planar NiN_2S_2 Complex of the Tetraanionic Form of the Ligand N,N'-Ethylenebis(*o*-mercaptobenzamide)

Jennifer C. DUTTON, Gary D. FALLON, and Keith S. MURRAY*
Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

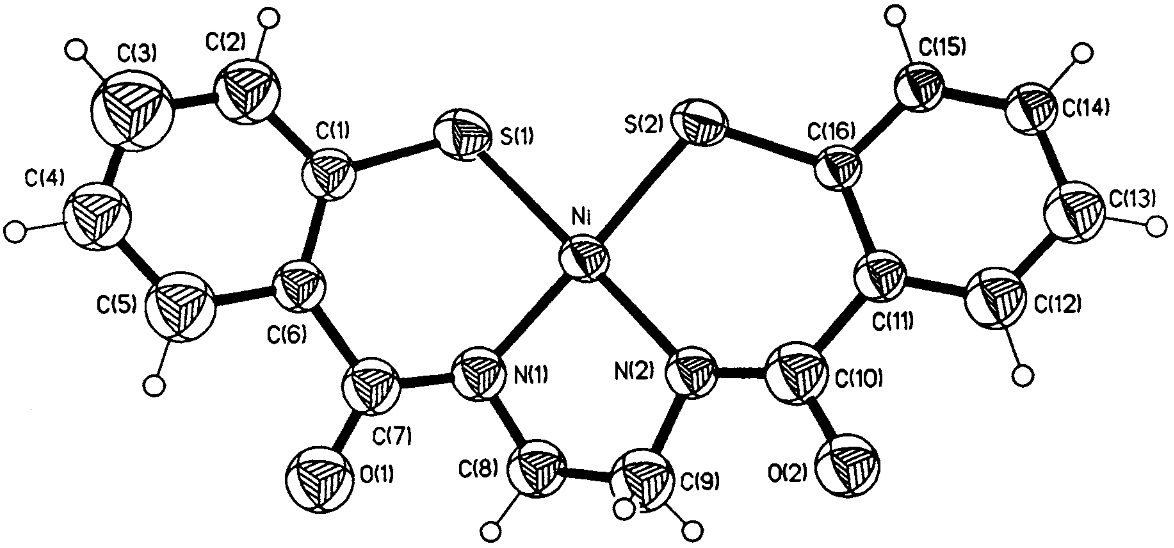
The X-ray crystal structure of a planar $[Ni^{II}N_2S_2]^{2-}$ complex containing the tetraanionic form of the ligand N,N'-ethylenebis-(o-mercaptobenzamide) is described. Comments are made in relation to a recent paper by Yamamura et al.,3) in which a binuclear $[Ni^{II}S_2O_2]_2$ derivative of the dianionic form of the ligand is described and to the earlier paper of Krüger and Holm5) who first described the present complex.

A recent series of papers by Yamamura et al. in this Journal1-3) prompts us to report one aspect of our own related work. Yamamura et al.1) have applied the method of Becher et al.,4) involving displacement of isobutene from the t-butyl protected thioether ligand (labelled ebbtb) by $NiCl_2$, to give improved yields of the $\{NiN_2S_2\}$ complex, Ni(tsalen). The structural and redox properties of this complex and of its imine-reduced analogue, Ni(ebmba), were reported.1,2) Subsequently, in studies of a related ligand system N,N'-ethylenebis(*o*-mercaptobenzamide) (labelled $ebtsaH_4$ and shown below) these workers obtained3) and structurally characterized, an interesting bridged bis-bidentate complex containing two $\{NiS_2O_2\}$ chromophores; $Ni_2(ebtsaH_2)_2$. Chelation to each Ni by the dianionic form of this ligand was found to be via the deprotonated



$ebtsaH_4$

thiol group and the oxygen of the protonated amide. Yamamura et al.$^{3)}$ appear to doubt that an earlier report by Holm and Krüger$^{5)}$ of Ni^{II} bonded to the tetraanionic form ebtsa^{4-}, in the complex $(Et_4N)_2$ [Ni(ebtsa)] did indeed contain a $\{NiN_2S_2\}$ chromophore. This present short paper removes such doubts and shows that Holm and Krüger's preparative route, using more basic conditions, does lead to formation of the planar (Ni(ebtsa)]$^{2-}$ moiety. We had prepared this Ni^{II} complex as part of a wider study of planar and tetrahedral Ni^{II} (and other metal ions) N_2S_2 chromophores within mononucleating and binucleating N,S-donor ligand systems of the tsalen type and mercapto-amide types.$^{6,7)}$



Ni-S(1) 2.161(7), Ni-S(2) 2.149(7), Ni-N(1) 1.90(2), Ni-N(2) 1.89(2), S(1)-C(1) 1.74(2), S(2)-C(16) 1.74(2), N(1)-C(7) 1.32(3), N(1)-C(8) 1.43(3), N(2)-C(10) 1.31(3), N(2)-C(9) 1.43(3), O(1)-C(7) 1.28(3), O(2)-C(10) 1.30(3)Å, S(1)-Ni-S(2) 85.2(3), S(1)-Ni-N(1) 92.8(6), S(2)-Ni-N(2) 96.0(6), N(1)-Ni-N(2) 86.1(8)°

Fig. 1. ORTEP structure of [Ni(ebtsa)]$^{2-}$. The Et_4N^+ and H_2O groups are not shown. Selected bond distances and angles are listed.

The complex $(Et_4N)_2[Ni(ebtsa)]3H_2O$ was prepared using the reported route5) and brown crystals suitable for X-ray diffraction studies were obtained on slow evaporation of the preparative solution. Crystal data: $C_{32}H_{58}N_4NiO_5S_2$, f.w. 701.7, monoclinic, space group $P2_1/n$, a = 13.052(4), b = 30.125(5), c = 9.499(2)Å, β = 99.062(8)°, U = 3688(1)$Å^3$, D_C = 1.26, D_M = 1.27(1) g cm^3, F(000) = 1512, μ = 6.8 cm^{-1} for Mo-K_α radiation (λ=0.7107Å), Temp=20(1)°. Philips PW1100 diffractometer with graphite monochromated Mo-K_α radiation with $6° < 2\theta < 50°$, scan range $\pm(0.70 + 0.2 \tan\theta)°$, scan rate 0.04° s^{-1}. 6493 unique data (±h, +k, +l), 1174 data observed ($I \geq 3\sigma(I)$). R=0.078, R'=0.073. An ORTEP drawing of the molecular structure of $[Ni(ebtsa]^{2-}$, shown in Figure 1, displays the expected planar cis-N_2S_2 coordination around Ni. Pertinent bond distances are compared to those of Ni(tsalen) and Ni(ebmba) in Table 1. The Ni-S and Ni-N bond lengths are essentially similar in these compounds. The C=O group, bonded to Ni in $Ni_2(ebtsaH_2)_2$, is marginally shorter than it is in its non-bonded, deprotonated amido form in $[Ni\ ebtsa]^{2-}$. The overall metal-ligand conformation and geometry in the present complex is similar to that found in the related $M\{N_2O_2\}$ amido-chelates studied extensively by Collins and coworkers8) in order to stabilize high oxidation states of transition metals.

Table 1. Bond distances (Å units) in $\{NiN_2S_2\}$ and Related Complexes

Complex	Ni-S	Ni-N	C-N	C-S	C-O	Ref.
$(Et_4N)_2[(Ni(ebtsa)].3H_2O$	2.161(7)	1.90(2)	1.32(3)b)	1.74(2)	1.28(3)	t.wa)
	2.149(7)	1.89(2)	1.31(3)	1.74(2)	1.30(3)	
$Ni_2(ebtsaH_2)_2$	2.125(1)				1.266(4)	3
	2.126(1)				1.253(5)	
Ni(tsalen)	2.174	1.85	1.29c)	1.70		1
	2.139	1.86	1.30	1.73		
Ni(ebmba)	2.164	1.949	1.482d)	1.765		2
	2.170	1.941	1.487	1.750		

a) t.w.: this work. b) Amido group. c) Imine group. d) Reduced imine group.

References

1) T. Yamamura, M. Tadokoro, and R. Kuroda, Chem. Lett., 1989, 1245. 2) T. Yamamura, M. Tadokoro, M. Hamaguchi, and R. Kuroda, Chem. Lett. 1989, 1481. 3) T. Yamamura, R. Kuroda, and M. Tadokoro, Chem. Lett. 1989, 1807. 4) J. Becher, H. Toftlund, and P. Olesen, J. Chem. Soc., Chem. Commun. 1983, 740. 5) H. -J Krüger and R.H. Holm, Inorg. Chem. 26, 3645 (1987). 6) J. Becher, H. Frydendahl, H. Toftlund, J.C. Dutton, K.S. Murray, E.R.T. Tiekink, L.F. Taylor, and O.P. Anderson, to be published. 7) P. Iliopoulos and K.S. Murray, J. Chem. Soc., Dalton Trans., 1988, 433. 8) F.C. Anson, T.J. Collins, T.G. Richmond, B.D. Santarsiera, J.E. Toth, and B.G.R.T. Treco, J. Am. Chem. Soc., 109, 2974 (1987).

(Received March 14, 1990)