

The planes defined by Hg(1), N(1), N(1ⁱⁱ) and Hg(1), N(2ⁱ), N(2ⁱⁱⁱ) in the Hg(1) tetrahedron, and by Hg(2), N(4ⁱ), N(4^v) and Hg(2), N(3), N(3^v) in the Hg(2) tetrahedron are not normal to each other but make angles of 80.4 (2) and 75.4 (2)° respectively. The N—Hg—N angles within the tetrahedron around Hg(1) vary from 90.7 (2) to 135.9 (3)°, those around Hg(2) from 92.7 (4) to 138.2 (4)°. The Hg—N bond lengths are significantly different, being 2.244 (9) (×2) and 2.365 (7) Å (×2) for Hg(1)—N, and 2.179 (10) (×2) and 2.416 (11) Å (×2) for Hg(2)—N, respectively. Whereas the shorter Hg—N bonds are close, the longer bonds are significantly larger than the sum of the corresponding covalent radii (1.48 Å for tetra-coordinated mercury, Grdenić, 1969). The angles between the shorter Hg—N bonds are larger [135.9 (3) and 138.2 (4)°] than the angles between the longer bonds [90.7 (2) and 100.3 (4)°].

The sulphate anions, located at the alternative diads, are bridged by the water molecules through hydrogen bonds O(1)···O(5), O(2)···O(5), O(3)···O(6) and O(4)···O(6) of 2.80 (2), 2.82 (2), 2.84 (2) and 2.83 (2) Å, respectively. The interatomic N···O dis-

tances (Table 2) of 2.80 (1) to 3.26 (1) Å indicate hydrogen bondings between the NH₂ groups and the SO₄ and H₂O O atoms, so that the structure consists of a three-dimensional network. The bond distances and angles in the sulphate ions and in the tn ligands are within expected values.

This work was supported by the Foundation for Scientific Research of SR Croatia, Zagreb.

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Acta Cryst. (1984). **C40**, 1838–1839

Structure of Bis[*N,N*-bis(2-hydroxyethyl)dithiocarbamato]nickel(II), C₁₀H₂₀N₂NiO₄S₄

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(Received 25 January 1984; accepted 12 July 1984)

Abstract. $M_r = 419.25$, $P2_1/c$, $a = 6.372$ (1), $b = 11.844$ (1), $c = 11.474$ (2) Å, $\beta = 93.56$ (2)°, $V = 864.3$ Å³, $Z = 2$, $D_x = 1.611$ Mg m⁻³, Mo K α , $\lambda = 0.71069$ Å, $\mu = 1.529$ mm⁻¹, $F(000) = 436$, $T = 293$ K, $R = 0.046$, $R_w = 0.047$ for 1551 unique reflections. The Ni atom is at $\bar{1}$ and is planar-coordinated to four sulphur atoms, with Ni—S(1) = 2.209 (1) and Ni—S(2) = 2.193 (1) Å, which agree with those in other (dithiocarbamato)nickel compounds. The molecules are held together through O—H···O hydrogen bonds.

Introduction. Crystal structures of dithiocarbamates of nickel(II) [Ni(S₂CNR₁R₂)₂] with various substituents

(R₁ and R₂) have been reported (Raston & White, 1976). In all these cases the substituents were not hydrophilic in nature. We have observed that the presence of hydrophilic substituents such as C₂H₄OH causes high reactivity in nickel dithiocarbamates towards substitution reactions. To see whether this is reflected in the bond parameters of the compound, we undertook the crystal structure analysis of the title compound.

Experimental. Bis[*N,N*-bis(2-hydroxyethyl)dithiocarbamato]nickel(II) prepared using an earlier method (Sejkan & Aravamudan, 1978). Single crystals obtained by dissolving compound in acetone–water and evaporating solution. Needle-shaped green crystal

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0.175 × 0.2 × 0.375 mm; Enraf–Nonius CAD-4 diffractometer; cell constants from least-squares analysis of 25 high-angle reflections; range of θ from 2 to 28°, h : 0 to 8, k : 0 to 15, l : -15 to 15; no absorption correction; insignificant fluctuations in two reflections (244, 226 monitored every hour); 1551 reflections with $I > 3\sigma(I)$ considered observed; $R_{\text{int}} = 0.03$ from merging 142 equivalent reflections. Structure determined using *SHELX76* (Sheldrick, 1976) and heavy-atom technique. Two hydrogen atoms fixed by geometrical constraints. Final $R = 0.046$, $R_w = 0.047$, $w = 1.00/[\sigma^2(F_o) + 0.0364|F_o|^2]$, number of parameters refined (based on F) 97, non-hydrogen anisotropic and hydrogen isotropic. Final difference Fourier map contained no peak higher than 0.73 e Å⁻³; $(\Delta/\sigma)_{\text{max}} = 0.98$. Atomic scattering factors from Cromer & Mann (1968) for non-H atoms, and Stewart, Davidson & Simpson for H; anomalous-dispersion-correction factors from Cromer & Liberman (1970).

Discussion. Positional and thermal parameters are listed in Table 1. Bond parameters are given in Table 2.* Fig. 1 shows an *ORTEP* plot (Johnson, 1976) of the molecule. The Ni atom lies at the centre of symmetry of the planar molecule bonded to four sulphur atoms of the two dithiocarbamate ligands. The molecular parameters of the NiS₄ unit differ very little from those of other dithiocarbamates of nickel(II) except where both R_1 and R_2 are hydrogens. In keeping with the X-ray result, infrared evidence also does not indicate any significant change in the C–N stretching frequency with respect to other dithiocarbamates. Therefore, the high reactivity of the present complex observed in substitution reactions is to be ascribed to the electronic effects of the hydrophilic C₂H₄OH groups.

The Ni–S distances lie in the expected range for four-coordinated diamagnetic complexes of nickel(II) (Cocouvanis, 1979). The S(1)–Ni–S(2) angle (79.25°) agrees with those found in similar compounds. NiS₂CN atoms are coplanar to within 0.05 Å. Oxygen atoms of the C₂H₄OH groups lie outside the coordination sphere of nickel. There are no Ni–Ni interactions. Bond parameters of the dithiocarbamate are found to be normal (Appa Rao, Seshasayee, Aravamudan & Radha, 1983).

The terminal oxygen atoms take part in hydrogen bonds as shown by the following parameters: O(1)···O(2) (\bar{x} , $y - \frac{3}{2}$, $\frac{1}{2} - z$) 2.711 (5) Å and O(1)–H(9)···O(2) 135 (6)°; O(2)···O(1) (x , $\frac{1}{2} - y$, $z + \frac{3}{2}$) 2.707 (5) Å, O(2)–H(10)···O(1) 157 (6)°.

* Lists of structure factors, anisotropic thermal parameters, hydrogen position parameters, least-squares-planes' parameters and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39633 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² × 10⁴ for Ni and S, and Å² × 10³ for others) for the non-hydrogen atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/(3\sin^2\beta).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ni	0	0	0	290 (2)
S(1)	−2958 (2)	−491 (1)	−974 (1)	339 (3)
S(2)	1014 (2)	−1526 (1)	−890 (1)	399 (3)
C(1)	−1547 (6)	−1640 (3)	−1426 (3)	29 (1)
N	−2305 (5)	−2488 (3)	−2066 (3)	31 (1)
C(2)	−4506 (7)	−2532 (4)	−2513 (4)	41 (1)
C(3)	5290 (13)	−2226 (6)	−3793 (5)	45 (3)
C(4)	9041 (7)	6547 (3)	7636 (4)	38 (1)
C(5)	9311 (8)	5702 (4)	8612 (4)	49 (2)
O(1)	−4018 (6)	−1129 (4)	−3997 (3)	66 (1)
O(2)	7334 (7)	5310 (3)	8978 (3)	62 (1)

Table 2. Bond lengths (Å) and bond angles (°)

Ni–S(1)	2.209 (1)	Ni–S(2)	2.193 (1)
S(1)–C(1)	1.728 (4)	S(2)–C(1)	1.713 (4)
C(1)–N	1.319 (5)	N–C(2)	1.464 (5)
C(2)–C(3)	1.510 (7)	C(3)–O(1)	1.396 (8)
N–C(4)	1.481 (5)	C(4)–C(5)	1.504 (6)
C(5)–O(2)	1.429 (7)		
S(1)–Ni–S(2)	79.3 (1)	Ni–S(1)–C(1)	85.2 (1)
Ni–S(2)–C(1)	86.0 (1)	S(1)–C(1)–S(2)	109.4 (2)
S(1)–C(1)–N	126.0 (3)	S(2)–C(1)–N	124.6 (3)
C(1)–N–C(2)	122.1 (3)	C(1)–N–C(4)	121.3 (3)
C(2)–N–C(4)	116.6 (3)	N–C(2)–C(3)	110.8 (3)
N–C(4)–C(5)	112.5 (3)	C(2)–C(3)–O(1)	112.1 (4)
C(4)–C(5)–O(2)	111.9 (3)		

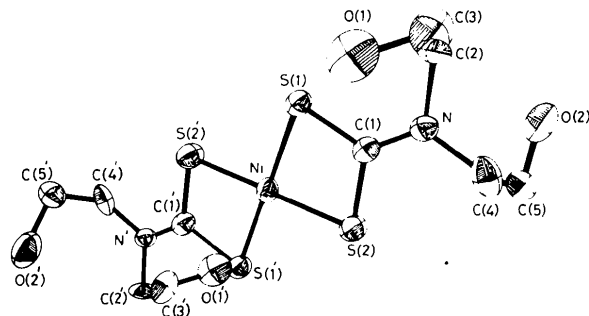


Fig. 1. Perspective view of the molecule.

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