

Refinement

Refinement on <i>F</i>	(Δ/σ) _{max} = 0.01
<i>R</i> = 0.0383	$\Delta\rho_{\text{max}} = 1.57 \text{ e } \text{\AA}^{-3}$
<i>wR</i> = 0.0428	$\Delta\rho_{\text{min}} = -1.85 \text{ e } \text{\AA}^{-3}$
<i>S</i> = 0.89	Extinction correction: none
1906 reflections	Atomic scattering factors
181 parameters	from <i>International Tables</i>
Only coordinates of H atoms	for <i>X-ray Crystallography</i>
refined	(1974, Vol. IV)
$w = 1/[\sigma^2(F)$	
$+ 0.00637F^2]$	

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \text{ (Hamilton, 1959).}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Pt	0.20831 (3)	0.11835 (2)	0.03934 (3)	2.37 (2)
S	0.0516 (2)	0.0878 (2)	0.0861 (2)	2.47 (8)
P	0.1852 (3)	0.2443 (2)	0.0636 (2)	3.0 (1)
Cl1	0.3654 (3)	0.1468 (2)	-0.0225 (2)	4.4 (1)
Cl2	0.2508 (3)	-0.0104 (2)	0.0186 (2)	3.9 (1)
O	-0.0316 (7)	0.1434 (5)	0.0686 (5)	3.6 (3)
C1	0.054 (1)	0.0646 (6)	0.1944 (6)	2.9 (4)
C2	-0.035 (1)	0.0784 (7)	0.2388 (8)	4.2 (5)
C3	-0.036 (2)	0.0577 (8)	0.3240 (8)	4.9 (6)
C4	0.049 (1)	0.0245 (8)	0.3597 (8)	4.7 (5)
C5	0.135 (1)	0.0105 (9)	0.3115 (9)	5.5 (6)
C6	0.140 (1)	0.0304 (9)	0.2298 (9)	5.0 (6)
C7	0.100 (1)	0.2662 (6)	0.1508 (9)	4.7 (5)
C8	0.096 (2)	0.3486 (7)	0.179 (1)	6.1 (7)
C9	0.306 (1)	0.2938 (8)	0.089 (1)	4.5 (5)
ClO	0.361 (2)	0.266 (1)	0.165 (1)	9. (1)
Cl11	0.129 (2)	0.2940 (8)	-0.0239 (9)	5.3 (6)
Cl12	0.179 (2)	0.282 (1)	-0.106 (1)	7.4 (8)
Cl13	0.008 (1)	-0.0024 (6)	0.0475 (6)	2.5 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Pt—S	2.212 (3)	S—C1	1.78 (1)
Pt—P	2.270 (3)	S—C13	1.79 (1)
Pt—Cl1	2.302 (3)	P—C7	1.82 (1)
Pt—Cl2	2.353 (3)	P—C9	1.82 (1)
S—O	1.475 (9)	P—C11	1.80 (1)
S—Pt—P	93.4 (1)	Pt—S—O	115.6 (4)
S—Pt—Cl2	91.4 (1)	Pt—S—C13	112.4 (4)
Cl1—Pt—Cl2	86.9 (1)	Pt—S—C1	111.7 (4)
Cl1—Pt—P	88.6 (1)	O—S—C1	110.4 (5)
S—Pt—Cl1	174.3 (3)	O—S—C13	107.2 (5)
P—Pt—Cl2	173.9 (1)	Cl—S—C13	97.9 (5)
Pt—P—C7	114.7 (4)	C7—P—C9	103.8 (7)
Pt—P—C9	113.2 (5)	C7—P—C11	104.7 (7)
Pt—P—Cl1	113.1 (5)	C9—P—C11	106.4 (7)

The structure was solved by analysis of the Patterson map (*SHELXS86*; Sheldrick, 1985) followed by difference Fourier syntheses and refinement using *SHELX76* (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 606–608

Redetermination of Bis(*N,N*-diethyl-dithiocarbamato)nickel(II)

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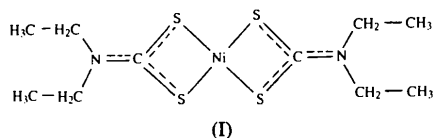
Abstract

The crystal structure of the α form of bis(*N,N*-diethylthiocarbamato-*S,S'*)nickel(II), [Ni(C₅H₁₀NS₂)₂], has been redetermined at 290 K by single-crystal X-ray methods. The Ni atom assumes a four-coordinate square-planar geometry with two isobidentate dithiocarbamate groups. The results confirm those of a previous study [Bonamico, Dessy, Mariani, Vaciano & Zambonelli (1965). *Acta Cryst.* **19**, 619–627] but are more precise.

Comment

The structure and chemistry of nickel(II) dithiocarbamates continue to be of interest. Three forms of bis(*N,N*-diethylthiocarbamato)nickel(II) have been reported (Bonamico, Dessy, Mariani, Vaciano & Zambonelli, 1965; Khan, Nazrul, Fackler, Murray & Heinrich, 1987). The structure of the α form, (I), was determined (Bonamico *et al.*, 1965) by photographic methods using Cu *K* α radiation to a final *R* factor of only 0.10.

The purpose of this redetermination, using diffractometric data collected with Mo $K\alpha$ radiation, was to obtain more accurate bond parameters. The results are summarized in Tables 1 and 2, and an ellipsoid view of compound (I) is shown in Fig. 1.



The near equality of the two Ni—S and two C—S distances confirms the isobidentate coordination of the dithiocarbamate group. Thus, the difference between the Ni—S1 and Ni—S2 bond lengths is only 0.006 (1) Å while the C1—S1 and C1—S2 distances differ by 0.001 (4) Å. For comparison, the corresponding differences are 0.012 (3) and 0.013 (10) Å, respectively, in the previous determination. The accuracy in the C1—N bond length of 1.324 (3) Å is an order of magnitude higher than that reported earlier [1.33 (10) Å].

The Ni atom lies on a centre of symmetry and participates in two short symmetrically related Ni...H contacts of 2.73 Å with H atoms attached to C2' [symmetry code: (i) $\pm(x, \frac{1}{2}-y, -\frac{1}{2}+z)$]. The torsion angles C2—N—C1—S2 [$-2.1(4)^\circ$], C2—N—C1—S1 [$178.5(2)^\circ$], C3—N—C1—S1 [$-4.5(4)^\circ$] and C3—N—C1—S2 [$174.9(2)^\circ$] confirm the near planarity of the S₂CNR₂ moiety.

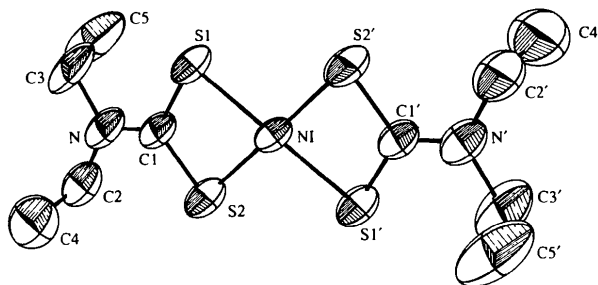


Fig. 1. A view of the title molecule showing 50% probability ellipsoids and the atom numbering. Primes indicate the symmetry operation $-x, -y, -z$. H atoms are omitted.

Experimental

The title compound was obtained following the method described by Bonamico *et al.* (1965). The density of the crystals was experimentally determined by flotation using heptane and carbon tetrachloride.

Crystal data

[Ni(C₅H₁₀NS₂)₂]
 $M_r = 355.25$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

Monoclinic

$P2_1/c$
 $a = 6.179(1)$ Å
 $b = 11.534(1)$ Å
 $c = 11.609(2)$ Å
 $\beta = 95.79(1)^\circ$
 $V = 823.2(2)$ Å³
 $Z = 2$
 $D_x = 1.434$ Mg m⁻³
 $D_m = 1.42$ Mg m⁻³

Cell parameters from 23 reflections

$\theta = 2-12^\circ$
 $\mu = 1.62$ mm⁻¹
 $T = 290$ K
Plate
 $0.38 \times 0.28 \times 0.13$ mm
Dark green

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
1711 measured reflections
1344 independent reflections
1115 observed reflections
[$I > 3\sigma(I)$]

$R_{int} = 0.024$
 $\theta_{max} = 25^\circ$
 $h = -7 \rightarrow 7$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 13$
2 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
 $R = 0.032$
 $wR = 0.033$
 $S = 0.61$
1115 reflections
79 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.002859F^2]$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.37$ e Å⁻³
 $\Delta\rho_{min} = -0.53$ e Å⁻³
Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni	0	0	0	0.0373 (2)
S1	0.3026 (1)	0.0460 (1)	0.1069 (1)	0.0470 (3)
S2	-0.0939 (1)	0.1665 (1)	0.0721 (1)	0.0498 (2)
N	0.2378 (4)	0.2459 (2)	0.2199 (2)	0.0493 (8)
C1	0.1618 (5)	0.1658 (2)	0.1448 (2)	0.0404 (9)
C2	0.1051 (6)	0.3476 (3)	0.2446 (3)	0.062 (1)
C3	0.4530 (5)	0.2340 (3)	0.2858 (3)	0.069 (1)
C4	0.1398 (9)	0.4474 (4)	0.1660 (4)	0.094 (2)
C5	0.4382 (7)	0.1759 (4)	0.4007 (3)	0.092 (2)

Table 2. Selected geometric parameters (Å, °)

Ni—S1	2.202 (1)	N—C2	1.476 (4)
Ni—S2	2.196 (1)	N—C3	1.472 (4)
S1—C1	1.714 (3)	C2—C4	1.498 (6)
S2—C1	1.715 (3)	C3—C5	1.504 (5)
N—C1	1.324 (3)		
S1—Ni—S2	79.4 (1)	S2—C1—N	124.7 (2)
Ni—S1—C1	85.1 (1)	S1—C1—N	125.2 (2)
Ni—S2—C1	85.3 (1)	S1—C1—S2	110.1 (1)
C2—N—C3	117.6 (3)	N—C2—C4	112.1 (3)
C1—N—C3	121.3 (2)	N—C3—C5	111.7 (3)
C1—N—C2	121.0 (3)		
S1—Ni—S2—C1	-1.7 (1)	C3—N—C1—S2	174.9 (2)
S2—Ni—S1—C1	1.7 (1)	C3—N—C1—S1	-4.5 (4)
Ni—S1—C1—N	177.2 (2)	C2—N—C3—C5	84.8 (4)
Ni—S2—C1—S1	2.3 (1)	C1—N—C3—C5	-92.3 (4)
Ni—S2—C1—N	-177.2 (2)	C1—N—C2—C4	-90.3 (4)
C2—N—C1—S2	-2.1 (4)	C3—N—C2—C4	92.6 (4)
C2—N—C1—S1	178.5 (2)		

Data reduction was carried out using *SHELX76* (Sheldrick, 1976). The coordinates of the non-H atoms were taken from Bonamico *et al.* (1965). All H atoms were included in the final cycle of refinement with $U(\text{H}) = 1.1U_{\text{eq}}(\text{C})$ and $\text{C}-\text{H} = 0.98 \text{ \AA}$. Geometry calculations were carried out using *PARST* (Nardelli, 1983). Neither absorption nor extinction corrections were considered necessary.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond angles involving H atoms, least-squares-planes data and torsion angles, complete with H-atom torsion angles, have been deposited with the IUCr (Reference: MU1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Coordination Polymer Reminiscent of the Pleated Sheets Observed in Polypeptides: Diaqua-(2,2'-bipyridine-3,3'-dicarboxylato)-copper(II)

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Abstract

The preparation and crystal structure of [Cu(BPDC)-(H₂O)₂] (BPDC = C₁₂H₆N₂O₄²⁻, the dianion of 2,2'-bipyridine-3,3'-dicarboxylic acid) are described. The Cu atom is pentacoordinate; the BPDC ligands and water molecules form a distorted square-pyramidal geometry about the metal atom, BPDC residues linking Cu atoms to give a coordination polymer with head-to-tail alignment [*i.e.* *catena*-poly[diaquacopper(II)- μ -

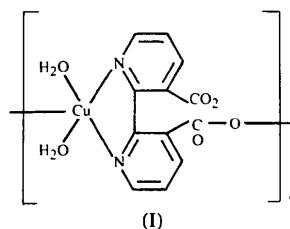
(2,2'-bipyridine-3,3'-dicarboxylato-*N,N'*:*O*)}]. Adjacent antiparallel chains are cross-linked by hydrogen bonds in a sheet-like structure reminiscent of the pleated sheets observed in polypeptides. The non-metallated O atoms of the carboxylate groups participate in hydrogen-bonding interactions with water molecules.

Comment

The use of metal complexes as probes of the structure of DNA has proved to be quite fruitful (Tullius & Dombroski, 1985; Sigman, 1986). Metal coordination complexes are also flexible reagents which permit observation of the effects of the central metal ion, the ligands and the coordination geometry on the binding event.

Square-pyramidal transition metal complexes usually adopt an octahedral configuration in solution by coordinating to a solvent molecule. In the solid state, the sixth coordination site can be filled by a ligand from an adjacent molecule, giving a coordination polymer (Chiang, Ho, Engen & Thompson, 1993). The head-to-tail nature of the coordination and organization in these materials is similar to that found in hydrogen-bonded systems. An advantage that coordination polymers may have over hydrogen-bonded systems is that the coordinate bond is typically much stronger than a hydrogen bond. The coordinate bond will also have a stronger directing influence on chain formation.

For these reasons, structural studies on metal complexes were undertaken in our laboratory (Ravikumar & Venkata Lakshmi, 1994). The title Cu^{II}-BPDC complex, (I) (where BPDC is 2,2'-bipyridine-3,3'-dicarboxylate), exists as an infinite coordination polymer in the solid state. A perspective view of the monomeric unit is shown in Fig. 1. Bond distances and angles (Table 2) are in good agreement with the values reported for related Cu^{II}-bipyridyl complexes (Stephens & Tucker, 1973; Newkome, Gupta & Fronczek, 1983; Goddard, Hemalatha & Rajasekharan, 1990).



The Cu atom adopts a five-coordinate geometry which may be described as distorted square pyramidal: it is bonded to two N atoms (N1 and N2) from one BPDC ligand, to two water molecules (O1W and O2W) and to a carboxylate O atom (O1ⁱ) from an adjacent BPDC residue [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$]. The base plane defined by the atoms N1, N2, O2W and O1ⁱ