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Redetermination of nickel bis(dithiocarbamate) at 100 K

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As part of our studies on Ni^{II} complexes, the structure of the title compound, $[Ni(CH_2NS_2)_2]$, was redetermined at 100 K. The crystal structure reveals a square-planar coordination geometry, with two dithiocarbamate ligands. The crystal packing is stabilized by N—H···S intermolecular interactions.

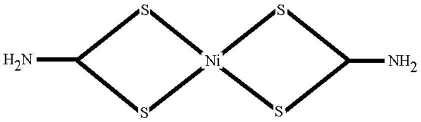
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(N–C) = 0.005 Å
R factor = 0.033
wR factor = 0.094
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of (I) was originally determined by Gasparri *et al.* (1967) using data measured from Weissenberg photographs. In the present redetermination, data were collected at low temperature, using a CCD area-detector diffractometer, in order to obtain more precise structural results.



(I)

As shown in Fig. 1, the structure of the title compound, (I), is composed of neutral $[Ni(S_2CNH_2)_2]$ complex molecules. The results show that the coordination around Ni^{II} is square planar, with four dithiocarbamate S atoms from two separate groups bonded to Ni [Ni—S1 = 2.2118 (9) Å, Ni—S2 = 2.2106 (9) Å, Ni—S3 = 2.2082 (10) Å and Ni—S4 = 2.2082 (10) Å]. The S—C bond lengths in (I) are between the mean values obtained for a single covalent bond (~1.64 Å) and a double covalent bond (≃1.76 Å) (Table 1), found in the September 2002 version of the Cambridge Structural Database (Allen, 2002) (see Figs. 2 and 3).

The structure is stabilized by intermolecular N—H···S hydrogen bonds between the NH_2 groups and the S atoms of neighbouring molecules (Table 2). These intermolecular interactions give rise to a three-dimensional network.

Experimental

Ammonium dithiocarbamate was prepared according to the literature (Booth, 1939) and mixed with a $nickel^{II}$ chloride aqueous solution. The brown crystals were recrystallized from ethanol. The IR spectrum showed the same bands as those reported in the literature (Nakamoto *et al.*, 1963).

Crystal data

$[Ni(CH_2NS_2)_2]$
M_r = 243.02
Monoclinic, $P2_1/c$
a = 7.1310 (4) Å
b = 12.9170 (8) Å
c = 10.9590 (5) Å
β = 130.293 (3)°
V = 769.95 (7) Å^3
Z = 4
D_x = 2.096 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6006 reflections
θ = 1.0–27.5°
μ = 3.51 mm^{-1}
T = 100 (2) K
Prism, brown
0.21 × 0.20 × 0.04 mm

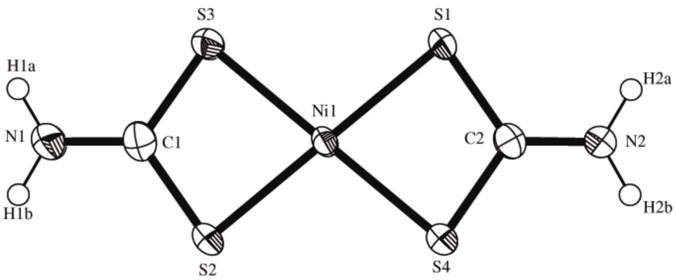


Figure 1
View of the title molecule, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.478$, $T_{\max} = 0.858$
4294 measured reflections
1355 independent reflections
1201 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 25°$
$h = -8 \rightarrow 8$
$k = -15 \rightarrow 13$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.094$
$S = 0.93$
1355 reflections
82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 1.443P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—S4	2.2082 (10)	S2—C1	1.728 (4)
Ni1—S3	2.2082 (10)	S3—C1	1.721 (4)
Ni1—S2	2.2106 (9)	S4—C2	1.726 (3)
Ni1—S1	2.2118 (9)	N1—C1	1.304 (5)
S1—C2	1.709 (4)	N2—C2	1.310 (5)
S4—Ni1—S3	176.68 (4)	C1—S3—Ni1	84.97 (13)
S4—Ni1—S2	100.30 (3)	C2—S4—Ni1	84.71 (13)
S3—Ni1—S2	79.71 (3)	N1—C1—S3	125.1 (3)
S4—Ni1—S1	79.44 (3)	N1—C1—S2	124.5 (3)
S3—Ni1—S1	100.36 (3)	S3—C1—S2	110.4 (2)
S2—Ni1—S1	176.81 (4)	N2—C2—S1	125.3 (3)
C2—S1—Ni1	84.98 (12)	N2—C2—S4	124.1 (3)
C1—S2—Ni1	84.73 (12)	S1—C2—S4	110.6 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···S4$^{\rm i}$	0.88	2.62	3.445 (4)	157
N1—H1*B*···S1$^{\rm ii}$	0.88	2.73	3.461 (4)	142
N2—H2*A*···S2$^{\rm iii}$	0.88	2.85	3.541 (3)	137
N2—H2*A*···S4$^{\rm iv}$	0.88	2.84	3.527 (4)	136
N2—H2*B*···S3$^{\rm v}$	0.88	2.66	3.538 (3)	178

Symmetry codes: (i) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1+x, y, 1+z$; (iii) $x-1, y, z-1$; (iv) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

H atoms were placed in calculated positions, with N—H = 0.88 Å and angles of 120°, and were included in the final cycles of refinement riding on their parent N atoms.

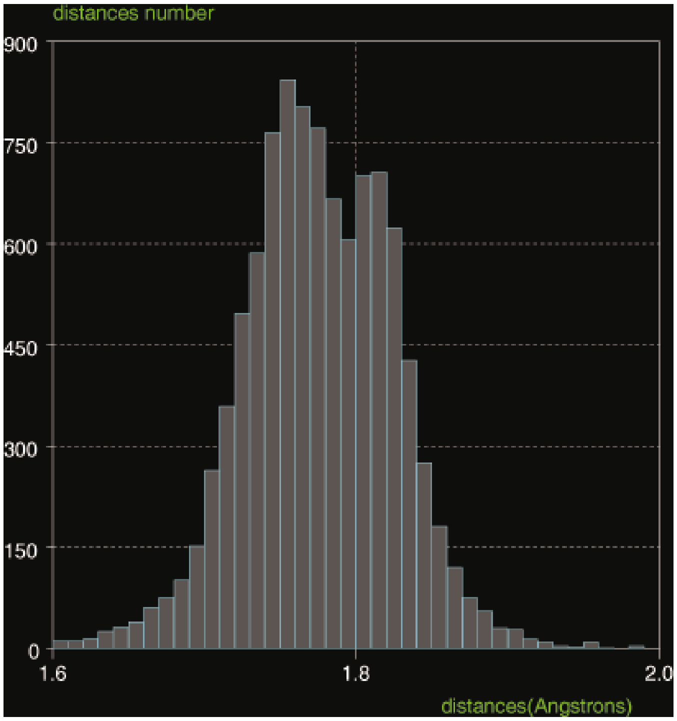


Figure 2
Distribution of the single S—C bond lengths.

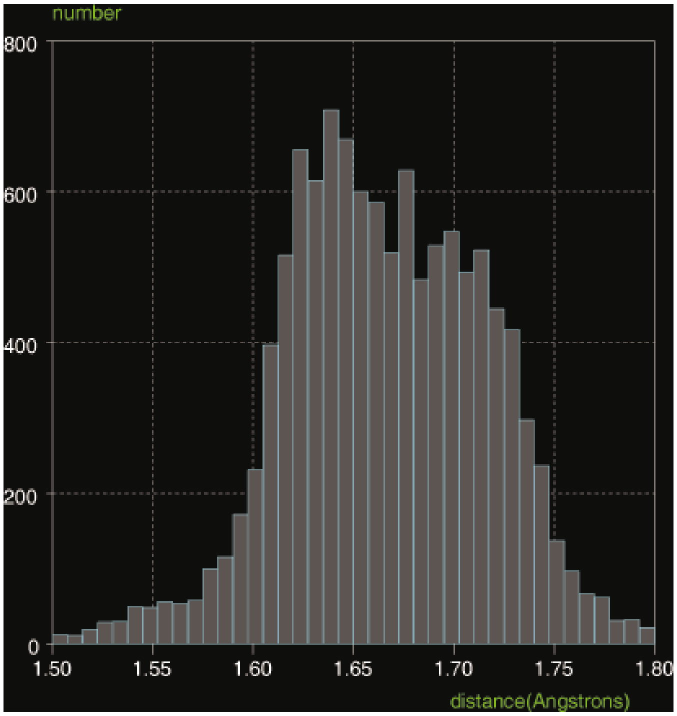


Figure 3
Distribution of double S—C bond lengths.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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