where Br_I^- is the standard bromide ion (at x, y, z), and Br_{II}^- is at $(\bar{x}, \bar{y}, \bar{z})$. The equal angles involving Br_{II}^-, and the very small angle (83°) involving Br_I^-, suggest that Br_{II}^- is hydrogen-bonded to N(2), distance 3·22 Å. The $Br_I^- \cdots$ N(2) distance (3·31 Å) is slightly shorter than the sum of the ionic radius of Br^- and van der Waals radius of nitrogen (3·45 Å). All the other intermolecular distances are normal; the shortest $Br^- \cdots$ N(1) contact is 3·93 Å.

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Structural Studies of Metal Dithiocarbamates.
I. The Crystal and Molecular Structure of the α Form of Nickel Diethyldithiocarbamate*

By M. Bonamico, G. Dessy†, C. Mariani‡, A. Vaciago and L. Zambonelli

Centro di Studio per la Strutturistica Chimica (CNR), Istituto di Chimica Farmaceutica e Tossicologica della Università degli Studi, Roma, Italy

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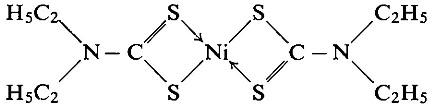
The crystal structure of the α form of nickel(II) bis(*N,N*-diethyldithiocarbamate), $[(C_2H_5)_2NCS_2]_2Ni$, at room temperature, has been determined by three-dimensional methods. There are two formula units in the monoclinic unit cell, $a = 6{\cdot}189$, $b = 11{\cdot}537$, $c = 11{\cdot}603$ Å, $\beta = 95°51'$, with space group $P2_1/c$. Each nickel atom occupies a centre of symmetry with the two ligand molecules planarly coordinated through the sulphur atoms. Three-dimensional anisotropic refinement by differential Fourier synthesis (final R value, 0·101) gave the bond lengths as Ni–S = 2·20, S–C = 1·71 and C–N = 1·33 Å, proved the planarity of the ligand molecule (obviously apart from the terminal CH_3 groups), and confirmed that $\cdots S_2C = NR_2$ is an important canonical form in the structure. The shortest intermolecular nickel contact is to a carbon atom at 3·54 Å.

Introduction

The structures of metal dithiocarbamates are being investigated because of (i) the fact that most of their detailed structures are unknown, (ii) the theoretical interest arising from the sulphur-containing four-membered rings present in these compounds, (iii) their biological (antifungal) activity, (iv) the lack of correlation between structural properties and the known chemical and physical properties of these compounds (Thorn & Ludwig, 1962).

The unusual features of this class of compound became apparent from the pioneering investigations of their physical and chemical properties carried out by Livio Cambi (Cambi & Malatesta, 1937; Malatesta, 1937; Cambi, 1941; and previous references quoted therein) who called our attention to the need for structural studies.

The first compound investigated in our laboratory was nickel(II) bis(*N,N*-diethyldithiocarbamate):



with the bond orders written in the conventional way. The first structural determination of a nickel salt had been that of Peyronel (1940 *a*, *b*), who published crystal data and a qualitative structure on the di-n-propyl derivative. Preliminary work (crystal data and two-dimensional structure analysis) had also been published on nickel(II) bis(*N,N*-diethyldithiocarbamate) by several research groups (Vaciago & Fasana, 1958; Pullia & Vaciago, 1960; Vaciago, Cabrini & Mariani, 1960; Shugam & Shkol'nikova, 1958; Shugam & Levina, 1960; Franzini & Schiaffino, 1963). Accurate data on bond lengths and angles, however, were still lacking.

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† Permanent address: Istituto di Chimica Generale e Inorganica della Università degli Studi, Roma, Italy.

‡ Permanent address: Istituto di Chimica Fisica della Università degli Studi, Milano, Italy.

Experimental

Crystal data

There are a stable monoclinic α modification and two less stable tetragonal ones, β and γ, of nickel diethyldithiocarbamate (Vaciago & Fasana, 1958).

The α form was examined in this work. The crystals are strongly pleochroic (green and dark red) monoclinic prisms, stable in air and in the X-ray beam. Detailed morphological and optical data can be found in the work of Franzini & Schiaffino (1963).

Crystals were obtained by recrystallization from chloroform. The unit-cell dimensions were determined by a modified, improved version of Christ's method (Mazzone, Vaciago & Bonamico, 1963) from zero-layer Weissenberg films about the *a* and *b* axes, with Cu *Kα* radiation (λ taken as 1·5418 Å). The crystal data given below replace those reported by us in previous publications (Vaciago & Fasana, 1958; Vaciago, Cabrini & Mariani, 1960). Note that cell dimensions tend to vary considerably, and β and γ modifications can be found more easily in presence of even slight impurities. The 070 reflexion may be present, with Cu *Kα* radiation, because of the Renninger effect (Pullia & Vaciago, 1960).

Nickel(II) *bis*(*N,N-diethyldithiocarbamate*)
$C_{10}H_{20}N_2NiS_4$. F.W. = 355·25 .
Monoclinic prismatic (but note $b^* \simeq c^*$, *i.e.* pseudotetragonal).
a = 6·189 ± 0·010, b = 11·537 ± 0·005, c = 11·603 ± 0·010 Å;
β = 95°51′ ± 5′; U = 824·2 $Å^3$;
D_m = 1·437 ± 0·05 $g.cm^{-3}$ (by flotation); Z = 2;
D_c = 1·431 $g.cm^{-3}$; $F(000)$ = 372.
Absorption coefficient for Cu radiation, 62 cm^{-1}.
Space group $P2_1/c$ (C_{2h}^5, No. 14), from systematic absences.

Intensity measurements

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *a* (6 layers) and *b* axes (4 layers) for approximately square crystals, 0·02 cm thick. 1376 reflexions were collected (about 73% of the possible ones with Cu radiation). The intensities were corrected for Lorentz and polarization factors, and placed on a common scale by the method of Rollett & Sparks (1960). No absorption or extinction corrections were applied.

Determination of the structure

The special Ni atom position (centre) was chosen as origin (0, 0 ,0) and the coordinates of all other atoms, apart from hydrogen, were found by Patterson and Fourier methods. Two-dimensional and generalized projection methods were used in the first stages, followed by three-dimensional Fourier syntheses. At this stage the reliability index *R* was 0·222.

Refinement

Refinement was done by differential Fourier synthesis. After three isotropic cycles, the reliability index *R* was 0·142 and three cycles of anisotropic refinement reduced *R* to 0·107.

At this stage electron density e.s.d. was 0·20 $e.Å^{-3}$. The introduction of hydrogen atoms in positions calculated to make the C–H bond lengths 1·09 Å and to complete tetrahedra around the carbon atoms brought the final *R* index to 0·101.

Table 1 gives the final atomic coordinates with their e.s.d.s (Cruickshank, 1949).

Table 1. *Final coordinates with standard deviations* $(\times 10)^4$

	x/a		*y/b*		*z/c*	
Ni	0000		0000		0000	
S(1)	3030	(3)	0467	(2)	1069	(2)
S(2)	−0929	(3)	1664	(2)	0723	(2)
N	2394	(13)	2450	(6)	2206	(6)
C(1)	1604	(12)	1658	(6)	1444	(6)
C(2)	1048	(18)	3465	(9)	2472	(9)
C(3)	4540	(17)	2338	(10)	2879	(10)
C(4)	1408	(27)	4458	(12)	1680	(14)
C(5)	4351	(24)	1722	(15)	4028	(12)

Anisotropic temperature factors with their e.s.d.s (Cruickshank, 1956) are listed in Table 2. In Table 3 atomic coordinates and isotropic temperature factors for hydrogen atoms are given.

The numbering of atoms is included in Fig. 1, except for the hydrogen atoms, which are numbered by reference to their respective carbon atoms.

Structure factors based on the final parameters and on the atomic scattering values recommended in *Inter-*

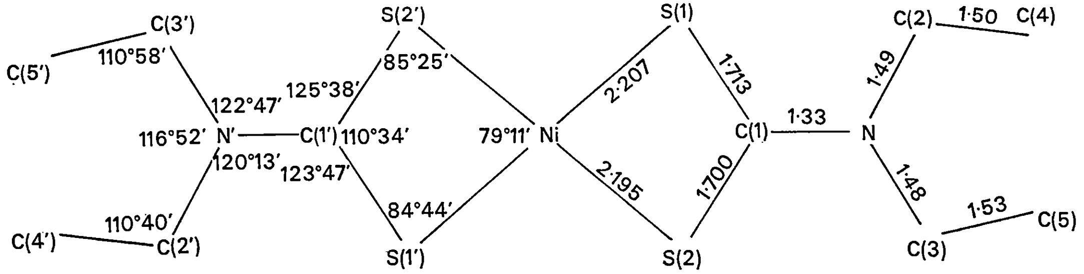

Fig. 1. Bond lengths (Å) and angles in the molecule of nickel(II) bis(*N,N*-diethyldithiocarbamate).

Table 2. *Thermal exponent coefficients* (*with e.s.d.s*)

b_{ij} as given here are defined by: $T=\exp\{-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	201 (5)	60 (1)	71 (1)	−6 (3)	23 (3)	−8 (2)
S(1)	217 (7)	70 (2)	90 (2)	13 (5)	17 (5)	−35 (2)
S(2)	231 (7)	75 (2)	90 (2)	44 (5)	10 (5)	−31 (3)
N	253 (29)	77 (6)	91 (7)	−40 (19)	64 (19)	−47 (10)
C(1)	198 (28)	68 (6)	76 (6)	−24 (18)	42 (18)	−17 (9)
C(2)	326 (41)	93 (9)	105 (9)	−17 (27)	100 (27)	−67 (14)
C(3)	275 (40)	111 (11)	125 (12)	−54 (30)	44 (31)	−94 (18)
C(4)	574 (76)	87 (11)	152 (16)	92 (39)	126 (49)	−7 (19)
C(5)	464 (66)	128 (15)	128 (14)	35 (44)	−85 (45)	−41 (21)

Table 3. *Coordinates* ($\times 10^4$) *and isotropic temperature factors for hydrogen atoms*

	x/a	y/b	z/c	B(Å^2)
H(2)*a*	1490	3732	3366	5·0
H(2)*b*	−0661	3219	2360	5·0
H(3)*a*	5220	3199	3051	5·0
H(3)*b*	5611	1840	2376	5·0
H(4)*a*	0964	4196	0784	7·0
H(4)*b*	3114	4709	1790	7·0
H(4)*c*	0408	5190	1889	7·0
H(5)*a*	3675	0858	3861	7·0
H(5)*b*	3287	2217	4537	7·0
H(5)*c*	5954	1650	4506	7·0

national Tables for X-ray Crystallography (1962) are compared with the observed structure amplitudes in Table 4. Correction for anomalous dispersion was applied for nickel and sulphur atoms (*International Tables for X-ray Crystallography*, 1962).

The observed and calculated values of electron density and second derivatives at the atomic peaks are compared in Table 5. Their e.s.d.s are:

$$\sigma(\varrho)=0{\cdot}20\ \text{e.Å}^{-3}$$

$$\sigma(A_{hh})=2{\cdot}08 \quad \sigma(A_{kk})=2{\cdot}27 \quad \sigma(A_{ll})=2{\cdot}11\ \text{e.Å}^{-5}$$

$$\sigma(A_{hk})=1{\cdot}30 \quad \sigma(A_{hl})=1{\cdot}32 \quad \sigma(A_{kl})=1{\cdot}33\ \text{e.Å}^{-5}$$

Calculations

The calculations were carried out on an IBM 1620 electronic computer.

Intensity corrections and structure factors were calculated with programs of V. Scatturin and co-workers. D. van der Helm's general Fourier synthesis for the

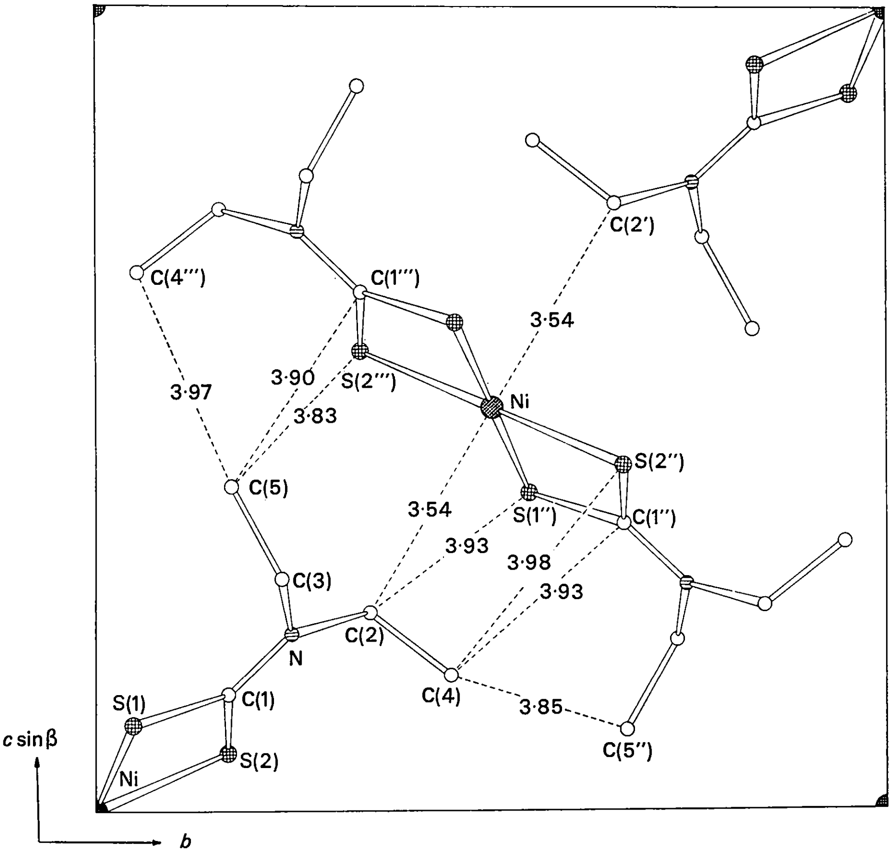

Fig. 2. Projection of the structure along [100]. The dotted lines show contacts of less than 4·0 Å.

Table 4. *Observed and calculated structure factors*

H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	82.0	75.9	-2	1	2	13.5	15.3	4	1	10	5.8	-6.9	2	2	7	26.0	-25.7	7	3	3	7.4	8.3
2	0	0	29.0	20.7	3	1	2	15.7	17.3	-4	1	10	3.6	4.0	-2	2	7	13.0	-11.0	-7	3	3	3.7	4.4
3	0	0	22.2	20.0	-3	1	2	15.4	15.1	5	1	10	6.9	-7.2	3	2	7	9.0	-8.9	0	3	4	8.7	-8.1
4	0	0	6.0	5.6	4	1	2	14.4	14.4	-6	1	10	3.2	4.2	-3	2	7	25.6	-25.6	1	3	4	35.1	34.4
5	0	0	25.1	-22.3	-4	1	2	10.4	-9.6	0	1	11	11.8	12.5	-4	2	7	6.0	-7.6	-1	3	4	35.6	35.1
7	0	0	10.0	10.8	5	1	2	20.4	22.0	-1	1	11	17.8	20.6	5	2	7	5.2	-4.8	2	3	4	5.4	5.4
0	0	2	21.8	16.0	-5	1	2	6.8	-8.2	2	1	11	5.6	5.7	-5	2	7	5.7	4.6	-2	3	4	38.5	-35.4
-1	0	2	96.2	102.3	-6	1	2	7.6	-7.7	-2	1	11	5.9	6.5	0	2	8	31.6	30.4	3	3	4	22.3	-22.3
2	0	2	60.4	61.1	-7	1	2	5.0	-6.7	3	1	11	9.3	8.5	1	2	8	27.0	25.0	-3	3	4	4.9	-2.4
-2	0	2	25.3	21.3	0	1	3	38.4	36.1	-3	1	11	11.9	13.2	-1	2	8	6.7	7.1	4	3	4	4.9	4.6
3	0	2	103.8	92.1	1	1	3	15.8	14.6	-4	1	11	13.2	15.5	2	2	8	4.3	4.8	-4	3	4	14.9	14.6
-3	0	2	3.6	-4.4	-1	1	3	87.3	87.1	-5	1	11	2.8	1.4	-2	2	8	19.7	19.5	5	3	4	6.4	6.0
4	0	2	2.6	-1.5	2	1	3	72.1	78.5	0	1	12	6.9	7.1	3	2	8	22.1	21.5	6	3	4	6.4	-6.5
-4	0	2	17.5	18.2	-2	1	3	16.6	13.3	1	1	12	7.2	8.5	-3	2	8	17.3	16.1	-6	3	4	5.6	-6.3
5	0	2	10.3	13.2	3	1	3	36.1	34.0	2	1	12	4.4	4.5	4	2	8	12.4	13.7	-7	3	4	4.7	5.1
-5	0	2	9.6	-9.4	-3	1	3	7.0	-7.5	-3	1	12	6.0	6.1	-4	2	8	3.6	3.5	0	3	5	21.6	19.0
6	0	2	12.6	13.0	4	1	3	3.6	4.0	-4	1	12	3.9	3.5	5	2	8	2.6	-1.9	1	3	5	32.8	31.2
7	0	2	6.3	-6.7	-4	1	3	25.7	24.9	0	1	13	3.8	4.3	0	2	9	13.8	15.0	-1	3	5	76.1	73.5
-7	0	2	18.9	17.0	5	1	3	17.4	19.7	1	1	13	4.7	5.9	1	2	9	2.7	-3.6	2	3	5	5.7	4.7
0	0	4	7.4	-7.1	-5	1	3	14.5	14.3	-1	1	13	9.9	12.1	-1	2	9	13.3	-18.1	-2	3	5	87.8	76.6
1	0	4	60.1	65.3	6	1	3	10.5	12.4	2	1	13	10.5	10.4	-2	2	9	8.7	-8.0	3	3	5	19.3	-18.1
-1	0	4	7.2	7.7	-6	1	3	3.9	-3.6	-2	1	13	5.9	6.2	4	2	9	12.0	-12.7	-3	3	5	36.5	30.9
2	0	4	90.1	91.8	7	1	3	5.4	-5.4	-3	1	13	2.8	-1.0	-4	2	9	4.6	-4.9	-4	3	5	7.9	8.3
3	0	4	33.0	32.8	-7	1	3	10.0	11.3	-4	1	13	4.1	5.1	5	2	9	8.4	-6.8	5	3	5	9.8	9.9
-3	0	4	20.5	-19.1	0	1	4	17.8	-21.9	0	1	14	3.1	-1.2	-5	2	9	9.6	8.9	-5	3	5	10.2	8.2
4	0	4	24.8	23.8	1	1	4	16.8	-17.6	-1	1	14	1.1	2.2	0	2	10	21.7	20.6	6	3	5	2.3	2.4
-4	0	4	23.3	20.6	-1	1	4	17.5	18.0	0	2	0	4.9	5.4	1	2	10	16.5	14.6	-7	3	5	4.1	-5.1
5	0	4	25.7	27.5	2	1	4	31.6	-32.0	1	2	0	32.4	34.0	-1	2	10	7.4	9.8	0	3	6	18.9	17.0
-5	0	4	22.7	25.9	-2	1	4	10.8	9.9	2	2	0	5.0	-3.3	2	2	10	11.6	11.1	1	3	6	5.6	6.3
7	0	4	9.6	-9.5	3	1	4	5.1	-4.0	3	2	0	55.4	62.7	-2	2	10	6.8	-7.2	-1	3	6	1.5	2.6
-7	0	4	7.5	9.6	-3	1	4	2.7	-3.4	4	2	0	22.5	24.0	3	2	10	17.9	16.5	2	3	6	25.9	-26.4
0	0	6	26.9	-27.9	4	1	4	10.2	8.5	5	2	0	5.7	5.9	-3	2	10	12.1	11.8	-2	3	6	10.6	9.4
1	0	6	36.1	37.1	-4	1	4	12.2	-12.8	6	2	0	20.5	23.2	4	2	10	3.3	4.0	3	3	6	6.0	6.4
-1	0	6	3.4	-6.3	5	1	4	9.5	9.9	0	2	1	26.9	-36.1	-4	2	10	5.5	6.7	-3	3	6	15.8	-14.8
2	0	6	17.4	17.8	-5	1	4	23.6	-25.4	1	2	1	18.2	20.3	0	2	11	2.4	1.8	4	3	6	14.0	13.4
-2	0	6	20.9	21.2	6	1	4	3.9	5.3	-1	2	1	13.9	-14.6	1	2	11	9.4	8.8	-4	3	6	4.4	5.2
3	0	6	12.1	11.7	-6	1	4	6.1	-8.7	2	2	1	38.1	37.6	-1	2	11	5.8	-6.5	5	3	6	6.2	-6.1
4	0	6	32.1	31.2	7	1	4	6.1	7.5	-2	2	1	25.7	25.4	2	2	11	8.7	8.8	-6	3	6	4.7	-3.7
-4	0	6	4.6	5.6	0	1	5	14.9	-17.0	3	2	1	30.8	31.4	-3	2	11	8.1	8.2	0	3	7	31.2	30.9
5	0	6	20.4	24.6	1	1	5	38.2	35.1	-3	2	1	41.2	43.2	4	2	11	5.5	-5.8	1	3	7	50.8	47.7
-5	0	6	30.2	36.9	-1	1	5	7.3	6.7	4	2	1	1.7	3.0	0	2	12	5.6	5.2	-1	3	7	18.2	17.5
-6	0	6	21.8	30.0	2	1	5	46.1	50.2	-4	2	1	2.7	2.8	-1	2	12	10.2	11.7	2	3	7	23.3	21.4
0	0	8	17.7	16.9	-2	1	5	38.5	37.0	5	2	1	14.2	14.6	2	2	12	11.2	10.2	-2	3	7	26.2	23.9
1	0	8	10.0	10.1	3	1	5	11.9	10.9	-5	2	1	2.3	-0.5	3	2	12	10.8	8.4	3	3	7	11.5	11.6
-1	0	8	3.4	-3.4	-3	1	5	1.7	-3.1	0	2	2	56.9	67.1	-4	2	12	8.4	8.5	-3	3	7	22.6	20.9
2	0	8	12.2	-15.0	4	1	5	21.6	22.4	1	2	2	29.8	-33.8	1	2	13	7.4	7.5	4	3	7	12.3	13.3
-2	0	8	18.3	17.1	-4	1	5	9.8	9.0	-1	2	2	59.5	64.3	2	2	13	4.7	3.8	-4	3	7	4.4	-4.8
-3	0	8	43.7	45.4	5	1	5	21.7	26.7	2	2	2	27.8	28.6	-3	2	13	8.4	6.7	5	3	7	4.6	-4.9
4	0	8	24.0	24.6	-5	1	5	29.4	31.8	-2	2	2	7.9	7.1	-4	2	13	6.0	7.5	6	3	7	6.0	-7.0
-4	0	8	5.0	6.3	-6	1	5	9.0	11.0	3	2	2	14.6	14.1	0	2	14	3.6	-3.5	0	3	8	10.4	9.6
5	0	8	6.9	7.7	0	1	6	5.8	-3.7	-3	2	2	34.8	32.8	1	2	14	3.1	3.7	1	3	8	12.0	-12.1
-5	0	8	7.4	7.6	1	1	6	14.3	-15.1	4	2	2	6.9	7.8	-1	2	14	2.0	2.9	2	3	8	4.6	4.7
6	0	8	7.1	9.7	-1	1	6	9.0	11.3	-4	2	2	61.9	57.1	-2	2	14	7.6	7.0	-2	3	8	5.4	5.3
-6	0	8	10.9	15.1	2	1	6	22.7	-23.1	5	2	2	11.0	12.0	1	3	0	25.1	-26.0	3	3	8	10.6	9.3
-7	0	8	5.4	8.0	-2	1	6	25.7	-26.3	-5	2	2	18.3	18.5	2	3	0	2.9	2.3	-3	3	8	5.5	-4.7
0	0	10	18.6	18.7	3	1	6	11.4	-13.5	6	2	2	20.5	22.6	3	3	0	3.7	2.8	4	3	8	3.7	-4.2
1	0	10	16.2	-15.9	-3	1	6	16.3	-16.3	0	2	3	75.8	-93.4	4	3	0	25.3	-24.0	-4	3	8	3.7	-3.9
-1	0	10	11.6	13.4	4	1	6	3.4	-4.5	1	2	3	9.5	-10.3	5	3	0	9.9	9.8	5	3	8	6.4	-5.6
2	0	10	5.7	-5.0	-4	1	6	4.3	-4.7	-1	2	3	44.8	41.9	6	3	0	7.4	7.7	-5	3	8	8.4	8.4
-2	0	10	12.0	12.3	5	1	6	3.4	2.5	2	2	3	4.3	4.7	7	3	0	5.0	-5.2	0	3	9	37.3	35.1
3	0	10	10.9	12.1	6	1	6	5.4	6.5	-2	2	3	12.1	10.8	0	3	1	16.4	19.3	1	3	9	24.8	23.8
-3	0	10	24.0	24.4	-6	1	6	5.8	-8.0	3	2	3	3.6	-4.1	1	3	1	38.8	-41.2	-1	3	9	8.6	9.1
4	0	10	0.9	3.1	0	1	7	14.5	13.3	-3	2	3	2.9	-0.6	-1	3	1	8.4	-11.8	2	3	9	18.8	19.2
-4	0	10	26.4	25.2	1	1	7	28.3	32.7	4	2	3	23.0	21.3	2	3	1	6.8	4.6	3	3	9	16.1	16.0
0	0	12	13.4	11.1	-1	1	7	10.0	-11.7	-4	2	3	12.0	-11.7	-2	3	1	22.4	21.6	-3	3	9	9.3	8.3
1	0	12	5.9	6.5	-2	1	7	29.2	29.3	5	2	3	17.3	18.6	3	3	1	35.4	38.9	4	3	9	7.6	8.7
-1	0	12	16.8	21.0	3	1	7	4.8	4.3	-5	2	3	26.5	-27.1	-3	3	1	59.7	54.1	5	3	9	4.7	-3.5
2	0	12	10.2	10.3	-3	1	7	28.3	26.2	0	2	4	12.1	-13.7	4	3	1	16.3	12.9	-1	3	10	8.1	-8.9
-2	0	12	7.9	9.2	4	1	7	23.8	24.5	1	2	4	14.5	15.0	-4	3	1	65.4	62.8	2	3	10	3.9	4.3
3	0	12	2.6	1.9	-4	1	7	5.0	5.0	-1	2	4	71.3	70.6	5	3	1	16.6	17.2	-2	3	10	9.3	8.8
-3	0	12	5.4	5.9	5	1	7	10.6	12.1	2	2	4	41.7	41.9	-5	3	1	21.8	21.5	3	3	10	3.6	2.5
4	0	12	6.3	-8.1	-5	1	7	15.1	17.2	-2	2	4	64.3	59.7	6	3	1	22.8	24.2	-3	3	10	7.9	8.3
-4	0	12	8.0	9.5	-6	1	7	16.3	18.9	3	2	4	8.1	6.5	-6	3	1	11.6	12.9	4	3	10	5.1	-4.9
0	0	14	5.2	5.7	0	1	8	7.5	8.1	-3	2	4	5.7	4.4	7	3	1	15.8	15.9	-4	3	10	6.2	-7.1
1	0	14	8.3	8.2	1	1	8	3.2	-4.7	4	2	4	6.4	-7.2	-7	3	1	8.8	9.7	5	3	10	3.8	3.0
-1	0	14	9.0	10.2	-1	1	8	20.2	-24.5	-4	2	4	22.7	23.1	0	3	2	43.9	-47.9	-6	3	10	3.2	4.0
-2	0	14	7.1	8.1	2	1	8	19.0	-21.2	5	2	4	17.3	19.3	1	3	2	6.9	-7.8	0	3	11	11.2	10.7
1	1	0	53.9	-58.5	-2	1	8	6.8	-6.9	-5	2	4	26.2	27.2	-1	3	2	31.2	-29.6	1	3	11	3.3	3.9
2	1	0	31.4	29.5	3	1	8	5.4	-4.3	0	2	5	7.0	-8.5	2	3	2	22.2	25.2	-1	3	11	5.6	6.0
3	1	0	22.9	25.1	-3	1	8	17.7	-19.2	-1	2	5	12.3	13.5	-2	3	2	2.0	-0.9	2	3	11	13.6	13.6
4	1	0	20.9	21.6	4	1	8	5.9	-6.9	2	2	5	24.9	-25.7	3	3	2	3.5	-2.9	-2	3	11	4.6	-5.7
7	1	0	7.2	-8.1	-4	1	8	9.2	-10.9	-2	2	5	10.2	-9.5	-3	3	2	25.1	21.8	3	3	11	18.6	15.5
0	1	1	71.0	99.4	5	1	8	6.1	-5.7	3	2	5	20.6	-20.1	5	3	2	7.5	6.8	-3	3	11	4.9	-5.2
1	1	1	36.1	43.3	-5	1	8	6.0	6.2	-3	2	5	22.8	-20.2	-5	3	2	25.3	-22.6	4	3	11	4.6	6.1
-1	1	1	63.0	67.8	-6	1	8	7.9	8.7	4	2	5	10.2	7.7	-6	3	2	7.0	6.9	-4	3	11	5.0	5.3
2	1	1	49.8	52.8	0	1	9	25.7	24.6	5	2	5	2.3	2.6	7	3	2	6.4	-6.4	0	3	12	6.9	-6.9
-2	1	1	26.8	-31.7	1	1	9	5.0	5.3	-5	2	5	12.7	-9.9	-7	3	2	4.7	4.8	-1	3	12	1.5	-2.9
3	1	1	69.6	66.1	-1	1	9	7.9	8.1	0	2	6	35.8	36.8	0	3	3	29.9	32.3	2	3	12	5.9	4.8
-3	1	1	24.6	21.4	2	1	9	8.4	-9.0	1	2	6	49.7	51.9	1	3	3	15.2	12.4	-2	3	12	6.9	-6.3
4	1	1	9.5	11.0	-2	1	9	9.3	8.5	-1	2	6	20.4	21.2	-1	3	3	73.8	72.4	3	3	12	3.6	-3.3
-4	1	1	22.7	24.4	3	1	9	14.2	14.5	2	2	6	21.3	18.5	2	3	3	12.8	11.4	-3	3	12	4.0	4.1
5	1	1	6.1	-6.2	-3	1	9	24.9	26.5	-2	2	6	49.6	49.2	-2	3	3	40.1	36.4	-4	3	12	2.7	3.6
-5	1	1	5.6	-7.4	4	1	9	9.6	10.6	3	2	6	13.5	-12.7	3	3	3	3.5	2.8	0	3	13	4.8	-4.9
6	1	1	13.3	15.2	-4	1	9	11.7	12.9	-3	2	6	28.2	26.7	-3	3	3	17.5	15.5	-1	3	13	2.3	3.5
-6	1	1	3.9	4.8	5	1	9	4.3	0.9	4	2	6	14.9	14.9	4	3	3	14.2	-14.6	2	3	13	7.2	5.8
-7	1	1	16.3	17.0	-6	1	9	7.6	10.1	5	2	6	9.2	9.6	-4	3	3	49.6	42.1	-2	3	13	6.3	5.4
0	1	2	45.8	-54.2	0	1	10	5.9	6.4	-5	2	6	12.2	10.2	5	3	3	16.6	16.2	-3	3	13	3.3	2.7
1	1	2	13.6	-15.2	1	1	10	2.6	4.6	0	2	7	16.3	15.1	-5	3	3	28.8	26.5	-4	3	13	5.8	6.0
-1	1	2	104.3	109.0	-1	1	10	7.5	-9.9	1	2	7	23.8	-22.7	6	3	3	17.7	19.1	1	3	14	3.5	3.5
2	1	2	54.3	54.3	2	1	10	12.2	13.4	-1	2	7	5.0	-6.1	-6	3	3	4.1	5.0	-1	3	14	4.1	5.0

Table 4 (*cont.*)

H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	4	0	41.1	38.8	-2	4	10	2.7	-0.6	4	5	7	11.6	12.0	1	6	6	10.6	9.4	-3	7	4	6.0	-4.3
1	4	0	2.7	-3.9	3	4	10	17.9	14.9	-4	5	7	12.0	11.6	-1	6	6	7.8	-10.0	4	7	4	6.9	5.9
2	4	0	5.4	3.4	4	4	10	2.7	5.2	5	5	7	10.7	10.0	2	6	6	13.0	13.2	5	7	4	12.7	11.7
3	4	0	34.4	36.1	-4	4	10	6.4	6.8	-5	5	7	9.9	10.4	-2	6	6	11.0	-12.9	-5	7	4	12.7	-12.1
4	4	0	44.6	40.1	-5	4	10	5.7	3.9	0	5	8	11.2	9.6	3	6	6	10.7	15.5	0	7	5	20.4	20.9
5	4	0	16.1	16.2	0	4	11	14.0	-14.1	1	5	8	5.8	-6.5	-3	6	6	17.9	16.6	1	7	5	13.3	13.9
0	4	1	15.6	16.5	1	4	11	12.1	-11.1	-1	5	8	9.1	10.7	4	6	6	23.2	20.0	-1	7	5	4.7	-7.0
1	4	1	19.2	-23.1	2	4	11	5.4	4.6	2	5	8	3.4	3.0	-4	6	6	23.2	19.4	2	7	5	15.6	18.9
-1	4	1	49.9	-49.7	-2	4	11	4.7	-4.2	-2	5	8	34.2	37.3	5	6	6	12.7	12.7	-2	7	5	4.5	-4.2
2	4	1	21.0	23.1	3	4	11	3.3	-3.2	3	5	8	23.5	21.4	-5	6	6	16.1	17.0	3	7	5	23.4	22.2
-2	4	1	12.3	-12.2	-3	4	11	4.5	3.7	-3	5	8	7.0	7.4	0	6	7	19.8	19.2	-3	7	5	13.0	11.7
3	4	1	34.0	-35.3	-4	4	11	3.3	-4.8	4	5	8	3.3	4.5	-1	6	7	4.7	5.8	4	7	5	16.7	15.0
-3	4	1	14.4	13.2	0	4	12	1.3	-1.5	-4	5	8	8.7	-9.2	2	6	7	8.7	-9.8	-4	7	5	13.4	13.2
4	4	1	38.5	-34.2	1	4	12	2.7	3.1	0	5	9	8.7	7.5	-2	6	7	15.8	17.1	5	7	5	5.0	4.7
-4	4	1	19.4	-18.2	-1	4	12	4.7	5.6	1	5	9	3.5	2.8	3	6	7	10.3	9.0	-5	7	5	8.4	8.4
-5	4	1	12.7	-12.2	2	4	12	8.4	7.3	-1	5	9	10.6	12.4	-3	6	7	9.6	-10.0	0	7	6	12.3	10.5
0	4	2	7.4	6.6	-2	4	12	4.5	3.9	-2	5	9	9.6	9.9	4	6	7	1.7	2.8	1	7	6	5.8	-5.8
1	4	2	9.1	10.8	3	4	12	7.8	5.4	3	5	9	10.6	8.5	-4	6	7	1.4	-2.4	2	7	6	34.5	-33.4
-1	4	2	65.7	64.1	-3	4	12	6.7	5.2	-3	5	9	13.9	12.1	5	6	7	9.2	-7.6	3	7	6	2.6	-3.2
2	4	2	22.1	23.9	-4	4	12	4.6	5.6	4	5	9	3.3	4.8	-5	6	7	6.1	6.3	-3	7	6	18.7	-18.6
-2	4	2	31.1	30.7	0	4	13	6.0	-6.2	-4	5	9	14.3	13.4	0	6	8	5.4	5.2	4	7	6	6.0	5.6
3	4	2	24.5	25.5	-1	4	13	2.7	4.1	5	5	9	6.1	5.7	1	6	8	5.8	-7.6	-4	7	6	3.6	-4.1
-3	4	2	31.4	28.5	-2	4	13	7.0	-6.6	-5	5	9	6.1	6.5	-1	6	8	18.5	18.3	0	7	7	11.8	10.5
-4	4	2	30.1	26.5	-3	4	13	4.1	-3.6	0	5	10	10.4	-11.1	-2	6	8	11.9	12.4	-1	7	7	18.9	19.8
5	4	2	10.4	9.7	-1	4	14	0.7	2.4	1	5	10	19.7	-16.8	3	6	8	8.7	5.8	2	7	7	3.9	3.1
-5	4	2	17.7	14.9	-2	4	14	4.5	4.7	-1	5	10	3.9	-6.2	-3	6	8	8.4	8.7	-2	7	7	9.0	8.1
0	4	3	17.8	17.8	1	5	0	62.1	-58.5	2	5	10	5.4	5.3	4	6	8	5.5	6.5	3	7	7	12.4	11.2
1	4	3	37.3	32.9	2	5	0	4.3	2.7	-3	5	10	7.0	6.9	-4	6	8	13.9	14.2	-3	7	7	11.1	11.8
-1	4	3	57.4	-44.0	4	5	0	31.6	-28.1	4	5	10	1.7	-2.6	5	6	8	10.4	9.2	4	7	7	3.3	3.5
2	4	3	7.9	8.3	5	5	0	8.7	-7.4	-4	5	10	5.5	-6.2	-5	6	8	11.5	11.0	-4	7	7	19.4	17.3
-2	4	3	72.0	-64.1	0	5	1	44.6	46.1	-5	5	10	5.7	-5.1	0	6	9	1.6	0.9	5	7	7	9.6	8.4
3	4	3	27.8	-32.1	1	5	1	36.3	42.4	0	5	11	2.4	3.5	1	6	9	18.0	-15.5	-5	7	7	6.9	7.8
-3	4	3	16.6	15.2	-1	5	1	58.3	55.3	1	5	11	3.1	3.6	-1	6	9	8.5	-10.6	0	7	8	5.4	5.6
4	4	3	13.9	-12.4	2	5	1	27.7	30.4	-1	5	11	8.2	10.6	3	6	9	7.0	5.8	1	7	8	12.9	-14.4
-4	4	3	29.7	25.9	-2	5	1	22.9	20.5	2	5	11	4.7	5.2	4	6	9	5.0	-5.7	-1	7	8	10.9	-12.2
5	4	3	4.6	4.4	3	5	1	21.2	23.0	-2	5	11	11.2	9.8	-4	6	9	12.0	-11.2	2	7	8	4.5	-5.0
-5	4	3	5.0	4.3	-3	5	1	18.7	16.5	-3	5	11	12.4	10.3	-1	6	10	7.4	9.7	-2	7	8	6.2	-6.4
0	4	4	31.7	33.7	4	5	1	14.9	14.6	-4	5	11	8.4	8.5	2	6	10	2.7	2.5	-3	7	8	12.4	-14.0
1	4	4	20.4	18.3	-4	5	1	4.6	4.5	0	5	12	10.6	-11.4	-2	6	10	17.3	17.6	4	7	8	6.9	-7.9
-1	4	4	37.0	31.2	-5	5	1	5.7	4.2	-2	5	12	5.6	-6.7	-3	6	10	17.6	18.0	-4	7	8	9.7	-9.8
2	4	4	20.3	19.5	0	5	2	15.7	-17.5	3	5	12	5.4	-4.6	4	6	10	0.4	2.0	5	7	8	6.9	-6.1
-2	4	4	38.4	33.9	1	5	2	22.1	24.6	-4	5	12	3.3	-4.2	-4	6	10	13.0	12.0	-5	7	8	6.9	6.8
3	4	4	9.3	-9.7	-1	5	2	40.1	-38.1	0	5	13	6.7	6.8	-5	6	10	6.9	6.7	-1	7	9	9.1	11.9
-3	4	4	35.4	25.5	2	5	2	11.6	11.8	1	5	13	6.3	6.0	0	6	11	7.9	-7.0	2	7	9	8.4	8.8
4	4	4	9.3	9.4	-2	5	2	55.3	-49.1	-1	5	13	4.3	6.5	-1	6	11	4.3	-6.3	-2	7	9	13.8	13.8
-4	4	4	26.0	21.8	3	5	2	30.6	-37.4	2	5	13	4.7	4.0	2	6	11	5.6	5.6	-3	7	9	7.5	8.0
5	4	4	15.6	15.1	-3	5	2	9.6	8.6	-2	5	13	7.9	7.0	-2	6	11	3.4	-3.6	4	7	9	2.3	3.3
-5	4	4	22.3	17.7	4	5	2	37.6	-30.8	-3	5	13	3.3	3.5	3	6	11	3.8	-2.5	-4	7	9	10.6	10.0
0	4	5	9.6	10.4	-4	5	2	0.9	-2.1	0	6	0	52.9	55.3	-3	6	11	4.5	3.9	-5	7	9	6.9	7.7
1	4	5	40.1	35.1	5	5	2	9.9	9.7	1	6	0	66.9	57.0	-4	6	11	0.9	-1.9	0	7	10	5.0	4.2
-1	4	5	34.6	32.6	-5	5	2	4.6	0.7	2	6	0	46.7	43.4	0	6	12	9.8	10.4	1	7	10	3.1	4.0
-2	4	5	7.6	-7.1	0	5	3	25.9	27.0	3	6	0	7.8	6.5	1	6	12	8.5	7.5	-1	7	10	10.2	-13.5
3	4	5	31.1	10.4	1	5	3	29.9	27.4	4	6	0	6.4	-7.4	-1	6	12	7.1	9.1	2	7	10	8.7	7.7
-3	4	5	9.0	-7.9	-1	5	3	22.8	21.1	0	6	1	21.7	-22.9	2	6	12	3.9	2.8	-3	7	10	3.6	4.5
4	4	5	20.0	17.8	2	5	3	33.1	39.8	1	6	1	5.5	-6.6	-2	6	12	11.0	11.0	4	7	10	6.0	-7.0
-4	4	5	25.1	20.9	-2	5	3	23.7	19.4	-1	6	1	33.0	-28.8	-3	6	12	4.5	4.7	-4	7	10	2.7	-3.9
5	4	5	8.0	-7.3	3	5	3	21.7	24.6	2	6	1	19.4	20.9	-4	6	12	3.3	4.5	0	7	11	5.6	5.6
-5	4	5	11.0	9.5	-3	5	3	11.1	9.5	-2	6	1	4.7	4.8	1	6	13	3.1	4.0	1	7	11	9.8	8.8
0	4	6	30.7	28.3	4	5	3	26.4	20.8	-3	6	1	26.0	22.9	-2	6	13	5.9	-5.4	-1	7	11	6.3	8.6
1	4	6	33.0	30.5	-4	5	3	8.7	8.4	4	6	1	20.0	-18.4	1	7	0	9.4	-10.9	2	7	11	2.5	3.1
-1	4	6	39.0	33.5	5	5	3	11.0	12.5	-4	6	1	9.3	-7.9	2	7	0	23.5	21.3	-2	7	11	12.3	12.7
2	4	6	15.6	15.8	-5	5	3	8.7	6.8	5	6	1	10.4	11.8	3	7	0	17.9	18.4	-3	7	11	6.0	5.7
-2	4	6	50.7	42.5	0	5	4	12.3	12.3	-5	6	1	8.7	-7.1	4	7	0	3.3	-1.9	-4	7	11	3.3	3.8
3	4	6	11.8	11.2	1	5	4	48.5	48.1	0	6	2	43.0	47.3	5	7	0	9.9	10.7	1	7	12	6.3	5.5
-3	4	6	9.9	9.3	-1	5	4	14.5	-12.7	1	6	2	42.5	43.3	0	7	1	28.9	28.5	-1	7	12	2.3	-3.0
4	4	6	6.0	5.4	2	5	4	3.9	3.6	-1	6	2	10.9	11.1	1	7	1	49.6	46.1	2	7	12	6.8	6.6
5	4	6	3.8	3.7	-2	5	4	6.4	-7.0	2	6	2	32.0	33.8	-1	7	1	27.1	24.9	-2	7	12	5.9	-5.5
0	4	7	22.2	22.6	3	5	4	12.1	-10.4	-2	6	2	13.8	13.5	2	7	1	26.3	25.8	-3	7	12	5.7	5.8
1	4	7	13.8	15.4	-3	5	4	12.1	10.8	3	6	2	22.4	25.8	-2	7	1	30.0	28.1	0	7	13	4.5	6.1
-1	4	7	12.9	14.2	4	5	4	13.4	14.4	4	6	2	31.6	26.0	3	7	1	8.1	6.9	0	8	0	7.0	-8.2
-2	4	7	27.4	30.1	-4	5	4	43.7	35.1	5	6	2	11.0	11.1	4	7	1	12.4	12.3	1	8	0	10.2	11.4
3	4	7	27.8	24.4	5	5	4	7.3	-7.2	0	6	3	16.9	-17.4	-4	7	1	4.6	-3.8	2	8	0	17.3	17.7
-3	4	7	4.8	5.2	0	5	5	14.5	13.1	1	6	3	14.2	14.9	5	7	1	8.4	10.4	3	8	0	5.7	5.8
4	4	7	3.6	5.1	1	5	5	24.8	23.2	-1	6	3	3.1	-3.2	-5	7	1	7.3	5.5	4	8	0	18.6	17.6
-4	4	7	4.1	5.5	-1	5	5	5.0	6.0	2	6	3	8.4	8.5	0	7	2	36.8	-40.3	5	8	0	21.1	20.4
5	4	7	9.6	-8.5	2	5	5	25.8	25.9	-2	6	3	27.7	-24.2	1	7	2	11.4	-14.5	0	8	1	11.9	-12.1
-5	4	7	9.9	11.7	-2	5	5	9.9	7.6	3	6	3	21.7	-22.1	-1	7	2	8.5	11.5	1	8	1	5.8	-6.3
0	4	8	25.3	22.1	3	5	5	20.9	22.0	-3	6	3	13.9	11.7	2	7	2	27.1	29.9	2	8	1	18.3	23.5
1	4	8	31.4	26.4	-3	5	5	8.1	6.5	4	6	3	6.0	6.2	-2	7	2	8.4	7.4	-2	8	1	11.6	11.5
-1	4	8	3.5	3.8	4	5	5	21.3	16.6	-4	6	3	17.1	15.7	3	7	2	7.5	7.0	3	8	1	11.8	12.6
2	4	8	12.3	13.1	-4	5	5	9.3	8.6	5	6	3	8.4	9.0	-3	7	2	26.3	22.3	-3	8	1	27.8	22.9
-2	4	8	9.3	7.0	5	5	5	12.2	11.6	-5	6	3	10.7	-9.0	4	7	2	13.9	13.2	4	8	1	2.3	3.5
3	4	8	12.1	11.1	-5	5	5	14.2	13.6	0	6	4	9.7	7.8	5	7	2	10.4	13.8	5	8	1	8.0	8.5
-3	4	8	17.3	19.2	0	5	6	18.7	18.9	1	6	4	39.0	34.7	-5	7	2	21.1	-20.8	-5	8	1	4.6	-3.3
4	4	8	8.4	10.0	1	5	6	16.9	15.5	-1	6	4	7.1	8.0	0	7	3	16.9	15.3	1	8	2	30.2	26.8
-4	4	8	5.5	5.1	-1	5	6	27.5	27.0	2	6	4	32.8	30.5	1	7	3	29.5	27.5	-1	8	2	4.3	4.8
0	4	9	5.2	-5.9	2	5	6	5.0	5.6	-2	6	4	7.0	5.4	-1	7	3	9.1	7.7	2	8	2	8.2	8.6
1	4	9	18.9	-15.0	3	5	6	15.7	12.1	3	6	4	35.1	43.0	2	7	3	14.6	14.6	-2	8	2	28.5	26.2
-1	4	9	2.3	-2.9	-3	5	6	13.5	-11.7	4	6	4	19.0	19.0	-2	7	3	16.4	14.8	-3	8	2	23.4	20.1
2	4	9	4.3	3.4	4	5	6	11.6	11.9	5	6	4	7.3	7.4	3	7	3	19.9	21.5	4	8	2	13.0	11.8
-2	4	9	20.1	21.4	-4	5	6	16.7	15.3	-5	6	4	7.3	5.3	-3	7	3	26.3	21.1	-4	8	2	5.0	4.3
3	4	9	11.8	10.8	5	5	6	12.2	-10.4	0	6	5	1.3	-3.0	4	7	3	25.1	22.2	5	8	2	5.2	5.8
-3	4	9	5.4	6.7	-5	5	6	13.8	14.8	1	6	5	15.0	16.1	5	7	3	3.8	3.6	-5	8	2	20.7	17.9
4	4	9	0.9	1.8	0	5	7	12.8	12.1	-1	6	5	30.2	28.0	-5	7	3	9.2	8.2	0	8	3	41.6	-40.3
-4	4	9	6.4	-7.4	1	5	7	8.2	9.0	2	6	5	11.0	-11.6	0	7	4	20.7	-19.9	-1	8	3	21.3	20.2
5	4	9	5.0	4.7	-1	5	7	2.0	2.9	-2	6	5	8.7	-7.5	1	7	4	9.4	9.7	2	8	3	2.5	2.5
0	4	10	17.5	17.2	2	5	7	7.9	8.3	-3	6	5	13.2	-11.8	-1	7	4	46.4	38.0	-2	8	3	3.9	-2.1
1	4	10	8.5	8.6	-2	5	7	11.0	10.8	4	6	5	13.0	11.8	2	7	4	7.6	-8.1	4	8	3	8.7	9.5
-1	4	10	8.5	11.2	3	5	7	11.1	9.8	-4	6	5	7.9	9.2	-2	7	4	14.6	-15.3	-4	8	3	3.6	-4.0
2	4	10	10.7	11.0	-3	5	7	14.2	13.3	0	6	6	1.3	2.0	3	7	4	15.1	-15.1	5	8	3	11.5	13.7

Table 4 (*cont.*)

H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	8	3	18.3	-16.5	-5	9	1	26.4	24.0	4	10	0	11.1	10.6	0	11	1	8.7	7.1	-4	12	2	9.3	-8.8
0	8	4	37.8	37.7	0	9	2	12.8	-12.1	5	10	0	16.8	16.8	1	11	1	25.6	25.8	0	12	3	1.3	3.6
1	8	4	12.9	13.1	1	9	2	7.4	8.8	0	10	1	2.0	2.0	-1	11	1	10.6	12.3	-2	12	3	3.6	5.0
-1	8	4	8.2	9.0	-1	9	2	2.0	3.4	-1	10	1	12.6	-12.9	2	11	1	11.6	11.8	-4	12	3	1.4	2.3
2	8	4	5.4	-6.0	2	9	2	9.6	10.6	2	10	1	3.9	-3.3	-2	11	1	23.2	24.1	0	12	4	15.0	13.6
-2	8	4	15.3	16.3	-2	9	2	9.0	-7.0	-2	10	1	9.0	-9.0	-3	11	1	3.6	3.2	1	12	4	10.2	11.4
-3	8	4	33.0	29.7	4	9	2	3.6	-4.1	3	10	1	10.3	-10.4	4	11	1	8.4	8.7	-1	12	4	4.3	-6.2
4	8	4	11.6	11.3	5	9	2	6.1	5.7	-3	10	1	5.4	-5.5	-4	11	1	3.3	-4.2	2	12	4	3.6	4.5
-4	8	4	9.7	10.1	-5	9	2	4.1	-3.1	4	10	1	13.0	-11.7	5	11	1	7.6	9.4	-2	12	4	5.6	-5.3
-1	8	5	8.2	10.1	0	9	3	20.0	18.1	-4	10	1	0.9	-3.0	-5	11	1	5.0	4.8	3	12	4	12.7	14.5
2	8	5	16.4	-18.1	1	9	3	14.5	16.8	-5	10	1	3.4	-3.4	0	11	2	14.4	13.2	-3	12	4	7.8	7.6
-2	8	5	4.5	-4.2	2	9	3	10.2	-11.7	0	10	2	14.5	13.7	1	11	2	1.1	2.2	-4	12	4	2.3	2.7
3	8	5	12.1	-12.1	-2	9	3	30.0	27.1	1	10	2	26.8	26.2	-1	11	2	16.5	-16.6	1	12	5	2.0	-4.0
-3	8	5	16.9	-16.6	3	9	3	3.8	-2.8	-2	10	2	20.3	19.5	2	11	2	6.8	-8.2	-2	12	5	5.0	5.0
4	8	5	9.3	8.2	-3	9	3	31.8	27.9	3	10	2	5.4	-5.9	-2	11	2	8.7	-8.6	-4	12	5	1.7	-2.4
-5	8	5	4.6	-4.5	4	9	3	10.2	9.1	-3	10	2	17.6	16.4	3	11	2	9.9	-8.0	0	12	6	1.4	1.4
0	8	6	23.3	21.3	-4	9	3	11.1	11.3	4	10	2	14.9	14.1	4	11	2	5.0	-5.5	1	12	6	3.9	-3.7
-1	8	6	27.5	25.2	5	9	3	2.9	3.6	-4	10	2	3.3	3.8	-4	11	2	3.3	4.2	-1	12	6	2.7	4.0
2	8	6	5.4	5.8	-5	9	3	9.2	8.0	5	10	2	6.4	7.3	5	11	2	3.8	-5.0	2	12	6	5.4	5.8
-2	8	6	12.3	13.7	0	9	4	2.1	1.7	-5	10	2	10.7	10.7	0	11	3	13.8	12.7	-2	12	6	8.4	-7.3
3	8	6	18.7	17.6	1	9	4	3.9	4.5	0	10	3	15.5	15.6	1	11	3	16.9	18.3	3	12	6	12.4	13.2
-3	8	6	17.3	15.2	2	9	4	6.2	-6.5	1	10	3	6.7	7.4	-1	11	3	2.0	-2.3	0	12	7	2.4	-3.1
-4	8	6	15.3	15.0	-2	9	4	6.8	-5.2	-1	10	3	8.5	-9.7	2	11	3	3.9	4.4	2	12	7	3.1	3.4
0	8	7	10.2	9.8	3	9	4	5.7	-5.5	-2	10	3	12.1	-12.1	-2	11	3	6.2	6.2	-3	12	7	2.9	3.2
1	8	7	12.9	-14.3	-3	9	4	6.3	-5.4	3	10	3	8.1	-7.8	3	11	3	11.5	12.0	0	12	8	2.0	-2.0
-1	8	7	4.3	-5.3	4	9	4	6.4	6.5	4	10	3	3.3	-2.5	-3	11	3	13.9	13.5	1	12	8	1.5	-2.4
2	8	7	11.9	-13.7	-4	9	4	1.7	3.0	-4	10	3	6.9	7.1	4	11	3	19.4	17.3	-1	12	8	4.7	7.2
-2	8	7	5.4	-5.9	-5	9	4	3.4	-3.6	-5	10	3	5.2	5.0	-4	11	3	3.6	-4.3	-2	12	8	5.0	5.6
-3	8	7	13.2	-13.4	0	9	5	31.9	30.9	0	10	4	23.0	21.8	0	11	4	6.4	6.5	1	13	0	4.3	5.8
4	8	7	2.7	-2.6	1	9	5	6.7	7.5	1	10	4	6.7	6.6	1	11	4	6.7	7.7	2	13	0	2.7	2.5
-4	8	7	6.9	-7.3	-1	9	5	32.7	30.0	-1	10	4	10.6	12.1	2	11	4	5.4	5.5	3	13	0	5.1	4.3
5	8	7	3.8	-3.1	2	9	5	8.2	-9.2	2	10	4	7.9	-9.2	4	11	4	0.9	-2.0	0	13	1	5.4	5.5
-5	8	7	5.7	5.3	-2	9	5	12.3	12.1	-2	10	4	13.0	13.9	-4	11	4	6.0	6.5	1	13	1	12.1	14.8
0	8	8	12.6	10.8	3	9	5	9.3	8.5	3	10	4	7.2	8.6	-5	11	4	6.4	8.6	-1	13	1	5.0	7.4
1	8	8	11.8	12.5	-3	9	5	23.0	24.4	-3	10	4	23.5	21.0	0	11	5	19.8	18.6	2	13	1	9.3	9.4
-1	8	8	15.0	16.2	-4	9	5	8.7	9.3	4	10	4	7.3	7.7	1	11	5	2.3	3.7	-2	13	1	10.2	9.2
2	8	8	17.5	19.0	5	9	5	5.2	-4.9	-4	10	4	1.7	2.7	2	11	5	7.0	6.5	-1	13	2	9.1	11.2
-2	8	8	5.4	5.2	-5	9	5	5.2	-5.0	0	10	5	7.4	7.1	-2	11	5	5.0	-5.0	-2	13	2	6.8	6.1
3	8	8	7.8	6.7	0	9	6	6.3	6.3	1	10	5	8.2	9.9	3	11	5	12.4	14.0	3	13	2	6.0	5.7
-4	8	8	8.4	8.3	-1	9	6	4.7	5.1	2	10	5	5.0	5.3	-3	11	5	8.1	7.2	-3	13	2	3.3	-3.0
0	8	9	8.0	7.4	2	9	6	2.0	-1.1	3	10	5	7.8	8.4	4	11	5	3.6	6.3	0	13	3	8.6	8.4
-1	8	9	11.4	-14.5	-3	9	6	5.4	-5.4	-4	10	5	4.6	5.5	-4	11	5	6.4	7.0	1	13	3	8.5	10.6
2	8	9	3.9	3.5	-4	9	6	8.4	2.5	-5	10	5	6.9	8.1	0	11	6	2.0	3.4	-1	13	3	2.3	-3.1
4	8	9	7.3	-7.8	-5	9	6	6.1	6.1	0	10	6	23.4	22.2	1	11	6	1.5	3.4	-2	13	3	5.0	5.4
-4	8	9	2.7	-2.8	0	9	7	21.3	19.3	1	10	6	1.1	3.0	2	11	6	6.4	7.2	3	13	3	4.8	6.3
-5	8	9	4.1	4.7	1	9	7	7.1	6.9	-1	10	6	14.2	15.8	-2	11	6	9.6	9.6	-3	13	3	7.5	8.2
0	8	10	5.0	4.2	-1	9	7	24.8	24.3	2	10	6	8.7	9.0	3	11	6	7.5	6.0	0	13	4	1.3	-1.7
1	8	10	12.6	10.8	2	9	7	18.0	19.4	3	10	6	11.1	10.3	-3	11	6	3.6	4.7	1	13	4	7.1	-9.9
-1	8	10	8.5	10.5	-2	9	7	5.6	6.2	-3	10	6	9.6	10.1	0	11	7	1.2	2.7	-1	13	4	1.5	2.4
2	8	10	9.3	9.1	3	9	7	11.5	9.4	-4	10	6	7.3	8.9	1	11	7	1.1	-2.9	2	13	4	2.2	-2.8
-2	8	10	9.6	9.1	-3	9	7	5.1	4.1	-5	10	6	5.2	-5.4	-1	11	7	9.1	11.4	-2	13	4	8.2	7.2
3	8	10	4.5	3.3	4	9	7	2.3	-2.6	0	10	7	1.3	2.6	2	11	7	7.0	6.7	0	13	5	6.4	6.7
-3	8	10	3.3	-3.4	-4	9	7	6.9	7.0	1	10	7	5.0	5.4	-2	11	7	1.3	-2.7	2	13	5	3.9	3.8
-4	8	10	0.4	0.5	-5	9	7	4.1	-3.4	2	10	7	5.9	5.6	3	11	7	10.8	9.5	-2	13	5	5.6	-5.5
1	8	11	4.7	5.1	0	9	8	7.5	6.5	-2	10	7	11.6	11.7	-4	11	7	8.4	9.7	0	13	6	3.5	-4.2
-1	8	11	2.3	-3.1	-1	9	8	6.3	-7.0	3	10	7	8.7	7.2	0	11	8	3.6	-3.4	-1	13	6	2.3	-4.3
2	8	11	8.2	7.7	-2	9	8	5.4	5.3	-3	10	7	3.8	4.3	-1	11	8	3.1	4.3	-2	13	6	3.1	-3.1
-2	8	11	3.4	-2.5	3	9	8	3.6	3.3	4	10	7	2.3	2.6	2	11	8	7.3	7.1	0	14	0	4.0	-3.5
-3	8	11	7.8	7.2	-4	9	8	2.7	-3.1	0	10	8	0.9	3.2	-2	11	8	4.5	4.0	1	14	0	2.7	4.2
1	8	12	8.5	8.3	0	9	9	4.8	4.3	1	10	8	3.1	4.5	-3	11	8	7.2	7.1	2	14	0	7.0	7.2
-2	8	12	3.9	3.7	1	9	9	14.5	12.5	-1	10	8	12.6	13.6	0	11	9	3.8	-4.0	0	14	1	1.9	-1.9
1	9	0	15.0	-15.0	-1	9	9	8.5	10.7	2	10	8	14.4	14.9	-1	11	9	4.7	6.1	1	14	1	1.1	2.9
2	9	0	4.3	3.3	2	9	9	18.7	17.3	3	10	8	9.0	8.1	-2	11	9	8.2	9.2	-1	14	1	6.3	8.4
3	9	0	5.4	5.7	-2	9	9	4.3	4.2	-3	10	8	5.1	-5.9	0	12	0	15.3	14.5	2	14	1	1.6	-1.9
4	9	0	4.6	-4.5	3	9	9	7.0	5.5	-4	10	8	6.0	6.9	1	12	0	18.9	19.4	-2	14	1	2.0	2.3
5	9	0	4.6	-3.7	-3	9	9	5.7	-5.6	0	10	9	4.1	-4.2	2	12	0	16.1	16.2	0	14	2	2.3	3.4
0	9	1	12.8	-13.0	0	9	10	3.6	-3.3	2	10	9	4.7	4.6	-1	12	1	3.9	5.5	1	14	2	4.7	6.1
1	9	1	6.3	6.7	2	9	10	7.0	6.3	-2	10	9	3.9	4.8	2	12	1	4.3	-4.9	-1	14	2	1.1	-0.8
-1	9	1	1.5	2.1	-3	9	10	7.0	6.1	-3	10	9	7.8	7.6	4	12	1	3.3	4.7	-2	14	2	4.3	5.1
2	9	1	5.0	4.8	1	9	11	12.6	10.4	1	10	10	12.1	10.6	0	12	2	9.2	8.7	1	14	3	3.9	-5.6
-2	9	1	30.5	31.2	-2	9	11	3.4	3.2	-2	10	10	6.8	6.3	1	12	2	23.6	22.9	-1	14	3	4.7	7.0
3	9	1	4.8	-5.1	0	10	0	23.7	-23.5	0	10	11	1.0	-5.2	2	12	2	11.2	10.8	-2	14	3	7.0	8.8
-3	9	1	17.9	17.5	1	10	0	5.8	7.4	2	11	0	5.0	-5.2	-2	12	2	13.0	12.7	0	14	4	7.2	7.9
4	9	1	16.7	15.1	2	10	0	22.6	23.3	3	11	0	6.0	-6.7	3	12	2	7.5	7.6	1	14	4	0.3	2.3
-4	9	1	14.9	13.2	3	10	0	6.7	6.6	4	11	0	5.5	-5.8	4	12	2	11.1	11.0	-1	14	4	1.5	5.4
5	9	1	13.8	16.4																				

Fourier syntheses, and E. Giglio's program for the differential Fourier syntheses were used. The least-squares planes were calculated by a program written by S. Chu (equation of the plane in the form $Ax+By+Cz=D$, referred to the crystallographic axes). Special modifications to the programs above and various minor other programs were written by one of us (L. Z.) and by A. Domenicano.

Discussion

Table 6 gives the bond lengths and angles with their e.s.d.s (Cruickshank & Robertson, 1953). Bond lengths and angles, with numbering of atoms, are also shown in Fig. 1.

The packing of the structure seen down the *a* axis is given in Fig. 2, showing van der Waals contacts of less than 4·0 Å. The shortest approach distance, 3·54 Å between the nickel atom and two carbon atoms [C(2), C(2')], is worth noticing, also for comparison with the nickel–sulphur contact of 3·41 Å in nickel xanthate (Franzini, 1963). The angles C(2)–H(2)*a*–Ni(0, $\frac{1}{2}$, $\frac{1}{2}$), S(1'')–Ni(0, $\frac{1}{2}$, $\frac{1}{2}$)–H(2)*a*, S(2'')–Ni(0, $\frac{1}{2}$, $\frac{1}{2}$)–H(2)*a* are 140° 19', 86°, 85° 8' respectively, with H(2)*a* in such a calculated position as to make the C–H bond length 1·09 Å and to complete a tetrahedron around the carbon atom.

All the atoms of the molecule (the asymmetric unit plus the centrosymmetrically related unit), apart from

Table 5. *Comparison of peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *from differential synthesis*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Ni	obs.	48·4	385	450	428	−7	33	−1
	calc.	48·2	389	452	434	−10	36	2
S(1)	obs.	29·4	243	282	255	8	14	−25
	calc.	30·0	249	288	265	8	20	−24
S(2)	obs.	28·6	234	265	241	12	12	−21
	calc.	29·3	242	277	252	11	17	−19
N	obs.	9·4	63	77	70	−3	8	−9
	calc.	9·5	64	77	71	−4	8	−9
C(1)	obs.	8·5	67	72	69	0	12	−4
	calc.	8·8	68	77	71	2	12	−3
C(2)	obs.	7·0	44	51	48	1	9	−10
	calc.	7·0	46	52	50	2	10	−10
C(3)	obs.	6·6	46	42	42	−1	0	−9
	calc.	6·9	47	46	47	0	2	−9
C(4)	obs.	5·6	30	36	30	2	0	−2
	calc.	5·8	33	38	33	2	0	−2
C(5)	obs.	5·4	33	30	34	0	1	1
	calc.	5·7	35	31	35	0	3	−1

Table 6. *Bond lengths and angles with standard deviations*

Ni–S(1)	2·207 Å	(0·002)
Ni–S(2)	2·195	(0·002)
S(1)–C(1)	1·713	(0·007)
S(2)–C(1)	1·700	(0·007)
C(1)–N	1·33	(0·010)
N–C(2)	1·49	(0·013)
N–C(3)	1·48	(0·017)
C(2)–C(4)	1·50	(0·015)
C(3)–C(5)	1·53	(0·022)
S(1)–Ni–S(2)	79° 11′	(11′)
Ni–S(1)–C(1)	84 44	(26)
Ni–S(2)–C(1)	85 25	(26)
S(1)–C(1)–S(2)	110 34	(37)
S(1)–C(1)–N	123 47	(46)
S(2)–C(1)–N	125 38	(46)
C(1)–N–C(2)	120 13	(58)
C(1)–N–C(3)	122 47	(1° 10)
C(2)–N–C(3)	116 52	(1 14)
N–C(2)–C(4)	110 40	(1 11)
N–C(3)–C(5)	110 58	(1 40)

the terminal CH_3 groups, lie approximately in a plane (calculated after Schomaker, Waser, Marsh & Bergman (1959) with all weights equal to 1 and determined by the equation: $-0·436x - 0·459y + 0·792z = 0$). The maximum and mean deviations from the plane are 0·10 and 0·05 Å respectively. The rather bad approximation to a plane is due mainly to C(2) and C(3) atoms, in accordance with the fact that the e.s.d.s for these atoms are much higher than for the others. In fact, if C(2), C(2′), C(3), C(3′) are excluded from the calculation of the best plane, maximum and mean deviations from the plane are 0·04 and 0·03 respectively. C(2) is at 0·05 Å from this plane and C(3) at 0·19 Å.

The bond lengths which are of special interest from a theoretical point of view are the bonds Ni–S (average: 2·20 Å), S–C(1) (average: 1·71 Å) and C(1)–N = 1·33 Å.

Each complex molecule is formed by two dithiocarbamic ligands planarly coordinated to a Ni atom through the sulphur atoms. This could also be inferred from the diamagnetic behaviour (Cambi & Malatesta, 1937) and from the crystal data. Distortions from exact flat square coordination with dsp^2 hybridization of the valence orbitals of the nickel atom, due to the strain in the four-membered ring, are noticeable in the valence angles. However, this strain has not resulted in any apparent increase in the nickel–sulphur or sulphur–carbon bond lengths.

Indeed, the Ni–S distance lies in the range 2·1–2·3 Å which is now accepted as the correct range of values for Ni–S bonds in four-coordinated, diamagnetic complexes of nickel, whilst the range 2·4–2·6 Å appears to be the correct one for Ni–S bonds in six-coordinated complexes. This observation is due to Lopez-Castro & Truter (1963) and it is supported, for instance, on the one hand by the values of 2·46 Å in tetra-thiourea-nickel(II) chloride* (Lopez-Castro & Truter, 1963), 2·51 and 2·57 Å in bis-thiourea-nickel(II) thiocyanate (Nardelli, Braibanti & Fava, 1957), and, on the other hand, by 2·16 Å in bis-thiosemicarbazidato-nickel(II) (Cavalca, Nardelli & Fava, 1962), 2·20 Å in the present work, 2·23 and 2·24 Å in nickel xanthate† (Franzini, 1963). As Lopez-Castro & Truter point out, 'these observations support the ligand-field theory which predicts that the stronger field produced by the ligands closer to the nickel will cause the d_γ electrons to pair in the d_{z^2} orbitals, so producing a diamagnetic complex which has no close neighbours in the z direction'. It is tineresting to note that the shorter the Ni–S bond distance, the longer is the contact distance in the d_{z^2} direction of nickel: 3·67, 3·54, 3·41 Å respectively for the three cases given above.

Also the S–C(1) bond length, 1·71 Å, compares well with the values found in thiourea and several of its derivatives and coordination complexes (Lopez-Castro & Truter, 1963; Dias & Truter, 1964; and other references quoted therein) and seems to be normal for a S–C(sp^2) distance.

As expected from previous infrared work (Chatt, Duncanson & Venanzi, 1956*a*, *b*), the C(1)–N bond,

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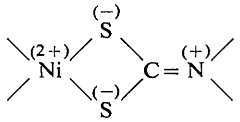
* From a preliminary two-dimensional analysis of this structure (Cavalca, Nardelli & Braibanti, 1956) the practically correct value of 2·45 Å had resulted.

† Two-dimensional analysis. The results are, however, consistent with Lopez-Castro & Truter's remark.

1·33 Å, has a high double bond character, *i.e.* there is a high contribution of the form:



to the true structure. In the LCAO-MO approximation the double bond order of this C–N bond can be said to be $p=0{\cdot}65$, as calculated by Coulson's formula for the C–C bond (Coulson, 1939) modified by Liquori & Vaciago for the C–N bond (Liquori & Vaciago, 1956; and, for a note on its validity, Favini, Mazzeo & Vaciago, 1963):

$$R=S-\frac{S-D}{1+0{\cdot}6625\,(1-p)/p}$$

where $S=1{\cdot}475$ Å, $D=1{\cdot}28$ Å.

The spectroscopic evidence that $\cdots\cdot\overset{(-)}{S_2C}=\overset{(+)}{NR_2}$ is an important canonical form in the structure of the dialkyldithiocarbamates, while $\cdots\cdot\overset{(-)}{S_2C}=\overset{(+)}{OR}$ makes only a minor contribution to the structure of the xanthates (Chatt, Duncanson & Venanzi, 1956 *a*, *b*) is confirmed by our results as compared with the value of 1·38 Å for the C–O distance in nickel xanthate (Franzini, 1963).

Our results are vastly different from those obtained by Shugam & Levina (1960), except for the nickel and sulphur coordinates; consequently we are unable to confirm the marked lack of planarity they observed [the Ni,S(1),S(2),C(1),N best plane is said to form an angle of 23° with the C(1),N,C(2),C(3) best plane] and furthermore their bond distances Ni–S=2·27, S–C(1)= 1·62, C(1)–N=1·26 Å are significantly different from the present ones. The CH_2 and CH_3 groups are given in very different positions from the ones we have found.

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