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The Crystal and Molecular Structure of Nickel(II) Bis(*N*,*N*-di-n-propyldithiocarbamate)*

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Nickel(II) bis(*N*,*N*-di-n-propyldithiocarbamate) is rhombohedral, space group $R\bar{3}$, with nine formula units in the hexagonal unit cell, $a=25{\cdot}20$, $c=8{\cdot}30$ Å. The crystal and molecular structure has been determined by three-dimensional Patterson and Fourier syntheses, and refined by isotropic and anisotropic least-squares methods, with a final R value of 0·075. Nickel is centrosymmetrically linked to two dithiocarbamic ligands, through four sulphur atoms; bond lengths: Ni–S 2·209 and 2·197, S–C 1·722 and 1·693, C–N 1·33 Å. The $\cdots S_2C=NR_2$ form gives, therefore, an important contribution to the molecular structure. The $(C_2NCS_2)_2Ni$ part of the molecule is nearly planar. The mean N–C bond distance of 1·47 Å corresponds to the single-bond value. The intermolecular distances of two CH_2 carbon atoms to one sulphur atom (3·75 and 3·68 Å) are shorter than the van der Waals $CH_2\cdots S$ contacts (3·85 Å). From the difference Fourier synthesis and from the $\varrho_o-\varrho_c$ values at the calculated positions the CH_2 hydrogen atoms were well localized; one of these shows a $CH\cdots S$ intermolecular interaction or hydrogen bond (2·88 Å).

Introduction

Dithiocarbamates have been the object in recent years of a growing interest because of their biological activity and their applications. Despite the large volume of literature on this class of compound (Thorn & Ludwig, 1962), many problems are still open regarding the relations of their physico-chemical and biological behaviour to their molecular structure. Owing to the fact that increasing the size of the alkyl group in the dialkyldithiocarbamates has an influence on some biological properties of these compounds, it may be of interest to compare the structures of homologous derivatives of the same metal.

A two-dimensional crystal structure analysis of copper(II) bis(*N*,*N*-di-n-propyldithiocarbamate) (Peyronel & Pignedoli, 1959*a*,*b*; Pignedoli & Peyronel, 1962) has shown a pyramidal pentacoordination of copper to five sulphur atoms through a coordinative dimerization of the molecule. A similar structure was found for copper(II) bis(*N*,*N*-diethyldithiocarbamate) (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). A three-dimensional analysis of copper(II) dipropyldithiocarbamate is now in progress in this Institute.

A preliminary study, with rotating crystal and trial-and-error methods, on nickel(II) bis(*N*,*N*-di-n-propyldithiocarbamate) was done some years ago (Peyronel, 1940, 1941), indicating the planar coordination of nickel to four sulphur atoms; the results of the present three-dimensional analysis of this complex may be compared with those recently obtained with the same method for the structure of nickel(II) bis(*N*,*N*-diethyldithiocarbamate) (Shugam & Levina, 1960; Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965).

Physico-chemical properties of the transition-metal dithiocarbamates were early studied by L. Cambi and L. Malatesta (Cambi & Coriselli, 1936; Malatesta, 1937, 1940*a*,*b* and further works).

Crystal data

Rhombohedral. The hexagonal cell has been used.
$a=25{\cdot}20\pm0{\cdot}03$, $c=8{\cdot}30\pm0{\cdot}02$ Å, $V=4564$ Å^3, $Z=9$
$d_{\text{exp}}=1{\cdot}337$ g.cm^{-3}, $d_{\text{calc}}=1{\cdot}3375$ g.cm^{-3}, $F(000)=1962$
Space group $R\bar{3}$ (no. 148) from observed general condition: $-h+k+l=3n$.

Intensity measurements and corrections

Intensities of *hkl* reflexions, with l from 0 to 5, were collected from a prismatic crystal about 0·39 mm in diameter, selected from several crystals, which frequently present twinning around the c axis. Intensities of 0*kl* reflexions were collected from a cut crystal about 0·30 mm in diameter.

The equi-inclination integrating Weissenberg technique, with multiple film, was used, recording 1327 independent reflexions, corresponding to about 58% of those possible with Cu $K\alpha$ radiation, and their intensities were measured photometrically. A first scaling of intensities was done by correlation of multiple films of each layer with their common reflexions and of the different *hkl* layers with their reflexions which are common to the 0*kl* layer. A final scaling of the different layers was done, with an independent scale factor K for each layer, after the introduction of the hydrogen atoms in the structure factor calculation, at the end of the isotropic least-squares refinement.

Corrections of intensities were made for Lorentz–polarization and absorption factors and for the spot size of the upper layers. Since there was evidence of

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the existence of a definite secondary extinction this effect was corrected at the end of an isotropic least-squares refinement (performed only with those reflexions having a value of sin $\theta/\lambda > 0{\cdot}35$, which are very little affected by secondary extinction) by using the method of Housty & Clastre (1957), based on the relation: $F_o = F_c \exp(-kI_c)$.

The secondary extinction has the maximum value in the *hk*0 plane and decreases almost regularly in the upper layers with the increase of the *l* value (Fig. 1). This method of secondary extinction correction, although less accurate than other more recent but more laborious methods (Åsbrink & Werner, 1966), may be considered sufficiently reliable in this case, using photographic data.

Determination and refinement of the structure

It was possible to find the correct orientation of the molecule only by means of three-dimensional Patterson syntheses; Ni, S(1), S(2), and C(0) positions were well identified and some evidence was obtained for the position of N, C(1), and C(2). By two- and three-dimensional Fourier syntheses, all the non-hydrogen atoms were located. A reliability index $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o| = 0{\cdot}20$ was obtained.

The atomic scattering factors of Hanson and coworkers (Hanson, Herman, Lea & Skillman, 1964) were used. Those of Ni and S were corrected for anomalous dispersion.

Table 1. *Positional parameters of non-hydrogen atoms in fractional coordinates* (× 10⁴) *and their estimated standard deviations* (Å)

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ni	5000	5000	0000			
S(1)	5402	4438	0778	0·002	0·002	0·002
S(2)	4213	4073	−0316	0·002	0·002	0·002
N	4508	3250	0769	0·007	0·007	0·007
C(0)	4679	3828	0432	0·009	0·008	0·008
C(1)	4930	3074	1466	0·010	0·010	0·009
C(2)	5222	2871	0159	0·013	0·012	0·012
C(3)	5615	2637	0984	0·013	0·014	0·013
C(4)	3866	2761	0513	0·009	0·009	0·009
C(5)	3488	2624	1986	0·010	0·010	0·010
C(6)	2818	2135	1665	0·010	0·010	0·010

The structure was then refined by the least-squares method for the positional parameters and isotropic temperature factors of each atom, using the reflexions with a value of sin $\theta/\lambda > 0{\cdot}35$ and introducing into the F_c calculation only the non-hydrogen atoms; these reflexions are practically unaffected by hydrogen atoms and by secondary extinction. The secondary extinction was then corrected in the manner described. At this stage an $R = 0{\cdot}116$ was obtained. Structure factors were then calculated by introducing the hydrogen atoms located in their theoretical positions, tetrahedrally bonded to the C atoms at a distance C–H of 1·09 Å, and assuming for the hydrogen atoms the isotropic temperature factors of the carbon atoms to which they were linked. After a few other isotropic least-squares cycles to refine only the positional and thermal parameters of non-hydrogen atoms, the reliability index came down to $R = 0{\cdot}095$.

Taking as fixed the calculated positional parameters and the assumed isotropic temperature factors for hydrogen atoms, the positional parameters and the anisotropic temperature factors of non-hydrogen atoms were then refined with three anisotropic least-squares cycles until the stationary condition was reached. The reliability index was then reduced to the final value, $R = 0{\cdot}075$.

The final positional parameters of non-hydrogen atoms with their e.s.d.'s (in Å) are given in Table 1;

Table 3. *Calculated positional parameters in fractional coordinates* (× 10⁴) *and assumed isotropic temperature factors for hydrogen atoms*

	x/a	y/b	z/c	B
H(11)	5289	3460	2130	4·8 Å²
H(12)	4684	2701	2321	4·8
H(21)	5512	3260	−0612	6·1
H(22)	4863	2503	−0551	6·1
H(31)	5972	3003	1696	7·6
H(32)	5326	2251	1756	7·6
H(33)	5825	2491	0058	7·6
H(41)	3664	2895	−0452	4·4
H(42)	3857	2346	0101	4·4
H(51)	3508	3042	2418	5·0
H(52)	3675	2464	2930	5·0
H(61)	2629	2298	0725	5·8
H(62)	2799	1714	1242	5·8
H(63)	2551	2042	2748	5·8

Table 2. *Thermal parameters of non-hydrogen atoms* (*and their e.s.d.'s*)

b, as given here, is defined by

$$T = \exp\{-10^{-5}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\}$$

	b_{11}		b_{22}		b_{33}		b_{12}		b_{13}		b_{23}	
Ni	229	4	202	4	1427	41	105	3	22	10	48	10
S(1)	232	5	230	5	1995	53	110	4	−43	12	67	12
S(2)	246	5	213	4	1651	56	105	4	−53	11	38	11
N	273	17	208	15	1509	151	131	13	−53	37	28	35
C(0)	266	19	206	17	1214	178	126	15	100	43	1	40
C(1)	329	24	257	21	1719	207	185	19	−16	53	77	48
C(2)	402	32	357	29	2930	284	232	26	2	72	19	69
C(3)	396	34	462	37	4083	356	288	31	−140	83	−158	87
C(4)	272	21	201	17	1276	186	98	16	−60	48	0	42
C(5)	283	22	250	20	1747	222	127	18	−57	53	−8	49
C(6)	303	24	241	21	1872	218	86	18	−6	53	36	50

Table 4. *Observed and calculated structure factors* (× 10)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	0	0	751	-851	5	14	0	1168	1126	17	3	-1	959	-966	21	10	-1	241	-241	11	0	2	441	-393
6	0	0	851	-955	8	14	0	983	967	19	3	1	177	-181	1	11	-1	703	-737	13	0	-2	285	225
9	0	0	865	977	11	14	0	350	-299	20	3	-1	256	-216	3	11	1	356	-387	14	0	2	989	1028
12	0	0	1154	1232	14	14	0	356	340	22	3	1	321	-303	4	11	-1	862	-894	16	0	-2	185	196
15	0	0	109	-114	3	15	0	130	-133	23	3	-1	124	77	6	11	1	992	-992	17	0	2	100	-150
18	0	0	544	540	6	15	0	403	-406	2	4	1	1795	2059	7	11	-1	777	-750	19	0	-2	109	14
21	0	0	174	-235	9	15	0	124	93	3	4	-1	1095	-1107	10	11	-1	297	308	20	0	2	336	287
24	0	0	303	306	12	15	0	85	14	5	4	1	809	-844	12	11	1	312	-288	22	0	-2	494	456
27	0	0	124	-136	15	15	0	227	-221	6	4	-1	1089	1122	13	11	-1	518	489	23	0	2	371	-340
4	1	0	1057	-1221	1	16	0	294	-302	8	4	1	2540	2561	16	11	-1	88	-187	0	1	2	5336	-5207
7	1	0	300	247	4	16	0	736	722	9	4	-1	871	-976	19	11	-1	77	-91	2	1	-2	759	-713
10	1	0	868	-897	7	16	0	412	-401	11	4	1	294	-302	2	12	-1	733	743	3	1	2	1866	-1943
13	1	0	836	-850	10	16	0	330	328	12	4	-1	1398	1443	4	12	1	244	-181	5	1	-2	386	-388
16	1	0	156	125	13	16	0	344	346	15	4	-1	371	414	5	12	-1	1704	1651	6	1	2	645	-506
19	1	0	453	-389	16	16	0	77	169	17	4	1	848	819	7	12	1	465	441	8	1	-2	1822	-1927
22	1	0	221	-223	2	17	0	759	-766	18	4	-1	359	356	8	12	-1	124	78	9	1	2	1160	-1142
25	1	0	297	295	5	17	0	247	-242	20	4	1	677	636	10	12	1	692	639	11	1	-2	291	-285
2	2	0	1363	1761	8	17	0	268	244	21	4	-1	130	-114	11	12	-1	241	-247	12	1	2	103	42
5	2	0	1589	1775	11	17	0	330	-328	23	4	1	115	-120	13	12	1	477	-438	14	1	-2	603	-621
8	2	0	1592	1705	14	17	0	68	-105	24	4	-1	79	98	14	12	-1	480	462	15	1	2	206	-219
11	2	0	509	-499	3	18	0	577	-601	1	5	-1	1422	1477	16	12	1	297	283	17	1	-2	927	-950
14	2	0	403	407	6	18	0	450	439	3	5	1	1110	1222	17	12	-1	127	-141	18	1	2	277	-318
17	2	0	415	411	9	18	0	127	-142	4	5	-1	1713	-1717	19	12	1	185	-165	20	1	-2	94	-21
20	2	0	659	597	12	18	0	156	-130	6	5	1	1186	-1189	2	13	1	309	-322	21	1	2	109	66
23	2	0	141	-150	1	19	0	132	93	7	5	-1	441	405	3	13	-1	954	-948	24	1	2	291	-301
3	3	0	1101	-1238	4	19	0	191	-137	9	5	1	815	-818	5	13	1	959	-933	1	2	2	1383	1327
6	3	0	1148	-1300	7	19	0	71	-17	10	5	-1	206	-174	6	13	-1	577	-545	3	2	-2	880	868
9	3	0	983	-1029	10	19	0	156	123	13	5	-1	271	-329	8	13	1	182	146	4	2	2	459	387
12	3	0	132	-86	2	20	0	889	851	16	5	-1	586	-629	9	13	-1	277	-277	6	2	-2	550	475
15	3	0	621	-597	5	20	0	421	-404	18	5	1	556	-528	12	13	-1	374	-371	7	2	2	291	-260
18	3	0	321	-306	11	20	0	127	52	19	5	-1	147	-153	14	13	1	235	-224	9	2	-2	233	169
21	3	0	309	-294	3	21	0	200	169	21	5	1	238	-254	15	13	-1	277	-277	10	2	2	1789	1881
24	3	0	147	-136	6	21	0	77	43	1	6	1	1710	-1860	1	14	-1	321	304	12	2	-2	1301	1392
1	4	0	130	138	1	22	0	156	-162	2	6	-1	465	-545	3	14	1	1383	1369	15	2	-2	132	128
4	4	0	256	-260	4	22	0	85	40	4	6	1	1704	1752	4	14	-1	674	668	16	2	2	74	29
7	4	0	2034	-1982	7	22	0	150	-171	5	6	-1	815	-788	6	14	1	1260	1237	18	2	-2	630	603
10	4	0	2914	2600	2	23	0	368	-349	7	6	1	1748	-1789	7	14	-1	365	-336	21	2	-2	132	-87
13	4	0	315	-278	5	23	0	50	59	8	6	-1	2037	2061	9	14	1	600	-536	22	2	2	706	696
16	4	0	244	265	3	24	0	206	207	10	6	1	1174	1157	10	14	-1	465	477	25	2	2	162	-162
19	4	0	227	205	6	24	0	132	170	11	6	-1	1127	-1141	12	14	1	439	408	1	3	-2	1327	-1297
22	4	0	333	326	1	25	0	185	-213	14	6	-1	162	181	13	14	-1	182	135	2	3	2	924	-937
5	5	0	1837	1892	4	0	1	2316	2429	17	6	-1	221	279	15	14	1	106	193	4	3	-2	777	-709
8	5	0	1154	-1246	5	0	-1	2043	-2271	20	6	-1	347	347	16	14	-1	235	242	5	3	2	430	439
11	5	0	862	-838	7	0	1	1489	1603	22	6	1	241	281	1	15	1	371	-385	7	3	-2	465	477
14	5	0	359	334	8	0	-1	1569	1679	2	7	1	718	828	2	15	-1	901	-868	8	3	2	97	-82
20	5	0	112	-121	10	0	1	2019	2048	3	7	-1	668	672	4	15	1	1062	-1059	10	3	-2	921	-986
23	5	0	174	-205	11	0	-1	536	525	5	7	1	983	1004	7	15	1	865	-842	11	3	2	1681	-1730
3	6	0	1416	-1519	13	0	1	127	-122	6	7	-1	433	389	10	15	1	338	294	13	3	-2	106	116
6	6	0	3408	2928	14	0	-1	209	271	8	7	1	124	-91	11	15	-1	362	-390	14	3	2	100	219
9	6	0	1213	-1149	16	0	1	506	500	9	7	-1	347	-393	14	15	-1	162	-183	19	3	-2	533	-487
12	6	0	565	594	17	0	-1	153	-161	11	7	1	244	-187	2	16	1	162	179	20	3	2	412	-411
15	6	0	100	25	19	0	1	389	-365	12	7	-1	135	128	3	16	-1	533	510	23	3	2	82	-101
18	6	0	365	360	20	0	-1	556	507	14	7	1	294	-285	5	16	1	359	-355	2	4	-2	700	-764
21	6	0	82	-46	22	0	1	627	556	15	7	-1	421	390	6	16	-1	1218	1178	3	4	2	1348	1346
1	7	0	718	-721	23	0	-1	327	-309	18	7	-1	327	-333	8	16	1	656	617	5	4	-2	118	278
4	7	0	589	-578	25	0	1	203	-200	20	7	1	185	186	9	16	-1	265	-273	6	4	2	1071	1099
7	7	0	324	-276	26	0	-1	88	138	21	7	-1	100	-144	14	16	1	82	93	8	4	-2	2808	2985
10	7	0	365	336	0	-1	1	1183	-1063	23	7	1	271	-241	15	16	-1	194	227	9	4	2	868	-871
13	7	0	565	555	2	1	1	4129	-3610	24	7	-1	132	196	1	17	-1	486	449	11	4	-2	1221	-1307
16	7	0	748	-712	3	1	-1	633	673	1	8	-1	965	-937	3	17	1	153	107	12	4	2	1118	1091
19	7	0	353	-359	5	1	1	1551	1628	3	8	1	1319	-1421	4	17	-1	497	-448	14	4	-2	424	440
22	7	0	268	256	6	1	-1	1480	-1645	4	8	-1	706	737	6	17	1	168	-157	15	4	2	347	301
2	8	0	1227	1279	8	1	1	1048	-1009	6	8	1	494	485	7	17	-1	233	-279	17	4	-2	106	55
5	8	0	680	-725	9	1	-1	2246	-2278	7	8	-1	868	-848	9	17	1	524	-474	18	4	2	180	144
8	8	0	909	860	11	1	1	1966	-2064	9	8	1	727	-682	10	17	-1	297	279	20	4	-2	383	400
11	8	0	636	-643	12	1	-1	736	-726	10	8	-1	627	606	13	17	-1	212	-221	21	4	2	97	-114
20	8	0	124	133	14	1	1	188	138	12	8	1	436	433	1	18	1	542	-539	1	5	2	933	-913
3	9	0	256	256	15	1	-1	230	-250	13	8	-1	527	-519	2	18	-1	347	295	3	5	-2	209	197
6	9	0	533	-505	17	1	1	606	-565	16	8	-1	247	304	4	18	1	686	685	4	5	2	1151	-1158
9	9	0	256	-267	18	1	-1	418	413	18	8	1	494	490	5	18	-1	633	-621	6	5	-2	1330	-1499
12	9	0	318	-291	20	1	1	185	-202	19	8	-1	424	-432	8	18	-1	253	261	7	5	2	503	434
15	9	0	497	475	21	1	-1	680	-626	21	8	1	150	-124	11	18	-1	138	153	9	5	-2	100	46
18	9	0	141	126	23	1	1	121	62	22	8	-1	112	-48	14	18	-1	53	-37	12	5	-2	433	435
21	9	0	188	-203	24	1	-1	233	-256	1	9	1	556	-622	2	19	1	277	-244	13	5	2	995	-965
1	10	0	1545	-1601	26	1	1	180	-216	2	9	-1	94	-37	3	19	-1	147	128	15	5	-2	203	-252
4	10	0	1631	1557	1	2	-1	1186	1094	4	9	1	259	229	5	19	1	121	44	16	5	2	600	-583
7	10	0	483	492	3	2	1	344	399	5	9	-1	492	-520	8	19	1	341	311	18	5	-2	268	-309
10	10	0	362	335	4	2	-1	374	344	7	9	1	353	304	9	19	-1	127	-125	19	5	2	256	-293
13	10	0	571	-532	6	2	1	544	459	8	9	-1	280	302	12	19	-1	65	-109	1	6	-2	556	568
16	10	0	550	515	7	2	-1	233	296	10	9	1	294	300	1	20	-1	359	-324	2	6	2	1972	2074
19	10	0	185	-185	9	2	1	439	350	11	9	-1	168	208	3	20	1	250	-229	4	6	-2	127	115
2	11	0	121	-138	10	2	-1	3249	2994	13	9	1	715	645	4	20	-1	444	420	5	6	2	2410	-2464
5	11	0	924	-970	12	2	1	2202	2217	14	9	-1	509	-544	7	20	-1	380	-371	7	6	-2	1616	-1737
8	11	0	153	110	13	2	-1	247	-265	16	9	1	165	-246	10	20	-1	88	89	8	6	2	1736	1825
11	11	0	150	110	16	2	-1	615	590	17	9	-1	156	86	1	21	1	215	186	10	6	-2	774	806
14	11	0	453	-436	19	2	-1	433	423	19	9	1	380	-380	2	21	-1	277	-247	13	6	-2	736	-742
17	11	0	168	-180	21	2	1	156	-131	20	9	-1	256	261	4	21	1	182	-210	14	6	2	106	-74
3	12	0	1089	1074	22	2	-1	483	524	2	10	1	400	462	2	22	1	362	333	16	6	-2	489	509
6	12	0	174	-132	24	2	1	288	327	3	10	-1	144	133	3	22	-1	209	-188	17	6	2	112	121
9	12	0	450	-451	25	2	-1	82	-38	5	10	1	347	362	1	23	-1	162	-201	19	6	-2	118	-144
12	12	0	624	595	1	3	1	1916	-2267	6	10	-1	483	479	3	23	1	77	92	20	6	2	453	472
15	12	0	182	-189	2	3	-1	589	-615	8	10	1	883	857	1	24	1	318	276	2	7	-2	671	686
18	12	0	206	221	4	3	1	1133	-1226	9	10	-1	742	-744	2	25	1	265	-260	3	7	2	786	808
1	13	0	162	-298	5	3	-1	559	600	11	10	1	904	-854	1	26	-1	277	282	5	7	-2	215	-227
4	13	0	456	-472	7	3	1	756	-724	12	10	-1	200	202	2	0	2	5457	4941	6	7	2	1045	-1066
7	13	0	986	-953	8	3	-1	1763	-1834	14	10	1	224	189	4	0	-2	1422	1495	8	7	-2	109	121
10	13	0	77	-35	10	3	1	1057	-1041	15	10	-1	109	-69	5	0	2	1451	1468	9	7	2	374	-354
13	13	0	197	-223	11	3	-1	474	-488	17	10	1	180	-205	7	0	-2	1257	1306	14	7	-2	347	-381
16	13	0	177	-170	13	3	1	1607	-1527	18	10	-1	403	425	8	0	2	338	262	15	7	2	447	482
2	14	0	115	-129	14	3	-1	124	149	20	10	1	144	141	10	0	-2	1754	1893	17	7	-2	127	208

Table 4 (*cont.*)

H	K	L	FO	FC
18	7	2	106	-41
21	7	2	433	-392
1	8	2	2552	-2709
3	8	-2	441	-415
4	8	2	1036	1066
6	8	-2	1251	1298
7	8	2	353	318
9	8	-2	724	-716
10	8	2	724	706
12	8	-2	100	65
13	8	2	338	-340
16	8	2	182	182
18	8	-2	306	330
19	8	2	82	62
1	9	-2	424	384
2	9	2	556	-597
4	9	-2	974	-981
5	9	2	168	225
7	9	-2	698	-720
8	9	2	562	-521
10	9	-2	550	532
11	9	2	115	137
13	9	-2	262	329
14	9	2	103	-23
16	9	-2	562	-572
17	9	2	247	-248
20	9	2	259	267
2	10	-2	1748	1857
3	10	2	854	-876
5	10	-2	135	77
8	10	-2	150	147
9	10	2	547	-533
11	10	-2	91	107
12	10	2	683	642
14	10	-2	359	343
15	10	2	418	-411
17	10	-2	227	-338
18	10	2	109	77
3	11	-2	1475	-1529
4	11	2	833	-786
6	11	-2	400	423
7	11	2	374	-387
9	11	-2	565	-542
12	11	-2	509	-475
13	11	2	235	221
15	11	-2	94	97
19	11	2	162	-168
1	12	-2	589	-562
2	12	2	180	148
4	12	-2	886	876
5	12	2	1124	1158
7	12	-2	689	608
8	12	2	1021	1012
10	12	-2	441	461
11	12	2	933	-871
13	12	-2	156	179
14	12	2	406	378
16	12	-2	394	421
2	13	-2	792	-751
3	13	2	365	-346
5	13	-2	912	-920
6	13	2	206	-169
8	13	-2	118	70
9	13	2	162	-191
11	13	-2	106	-55
14	13	-2	100	-246
15	13	2	103	-25
1	14	2	153	153
3	14	-2	712	703
4	14	2	233	-235
6	14	-2	515	502
7	14	2	82	-52
9	14	-2	536	-557
10	14	2	680	644
12	14	-2	418	407
13	14	2	97	-58
15	14	-2	88	122
16	14	2	230	213
1	15	-2	262	262
2	15	2	421	430
4	15	-2	1027	-1000
5	15	2	621	-654
8	15	2	698	-477
10	15	-2	250	-184
11	15	2	177	-193
13	15	-2	430	-449
14	15	2	244	-279
16	15	-2	62	56
2	16	-2	433	412
3	16	2	115	-52
5	16	-2	383	-362
6	16	2	939	939
8	16	-2	297	336
9	16	2	333	-276
11	16	-2	77	61
12	16	2	71	19
3	17	-2	515	524
4	17	2	227	-184
6	17	-2	127	87
7	17	2	327	-292

H	K	L	FO	FC
9	17	-2	79	-112
10	17	2	109	149
1	18	-2	124	27
2	18	2	901	905
4	18	-2	633	591
5	18	2	127	-112
7	18	-2	662	-647
8	18	2	115	130
11	18	2	156	194
2	19	-2	383	-410
5	19	-2	312	256
6	19	2	100	-69
9	19	2	209	-201
1	20	2	494	-514
3	20	-2	656	-637
6	20	-2	306	273
1	21	-2	138	-40
2	21	2	394	-388
4	21	-2	88	48
8	21	2	209	222
2	22	-2	421	419
3	22	2	109	128
4	23	2	221	-220
0	25	2	171	-150
0	0	3	3079	2951
3	0	3	1095	1129
3	0	-3	1489	-1411
6	0	3	1401	-1410
6	0	-3	2331	2326
9	0	3	403	-389
9	0	-3	394	394
12	0	3	1869	1951
12	0	-3	595	555
15	0	3	556	-508
15	0	-3	324	286
18	0	-3	662	618
21	0	3	147	-154
21	0	-3	147	99
24	0	3	300	310
1	1	3	989	-1019
1	1	-3	980	-1043
4	1	3	1113	-1269
10	1	3	459	-440
10	1	-3	1024	-1038
13	1	3	1454	-1465
13	1	-3	439	409
16	1	-3	595	-581
19	1	3	377	368
19	1	-3	1080	-1033
22	1	3	144	-162
22	1	-3	180	196
2	2	3	2711	2657
2	2	-3	497	371
5	2	3	135	187
8	2	3	1369	1413
8	2	-3	2358	2464
11	2	3	162	161
11	2	-3	995	-1032
14	2	3	948	960
14	2	-3	689	673
17	2	-3	277	251
20	2	3	480	443
20	2	-3	447	440
23	2	3	285	-280
3	3	3	2151	-2114
3	3	-3	892	875
6	3	3	94	72
6	3	-3	427	-428
9	3	3	1065	-1021
9	3	-3	274	-217
12	3	3	162	-182
12	3	-3	995	-960
15	3	3	427	-464
15	3	-3	650	-655
18	3	3	630	-578
21	3	3	150	-79
21	3	-3	259	-271
1	4	-3	859	-830
4	4	3	2260	2175
4	4	-3	265	213
7	4	3	503	-472
7	4	-3	256	-269
10	4	3	1301	1325
10	4	-3	1339	1374
13	4	3	806	798
13	4	-3	194	-161
16	4	3	127	-267
16	4	-3	650	662
19	4	3	147	-167
19	4	-3	162	-72
22	4	3	450	469
2	5	3	297	-310
2	5	-3	518	448
5	5	3	180	157
5	5	-3	621	563
8	5	3	421	-374
8	5	-3	527	-435
11	5	3	1133	-1075
11	5	-3	253	164
14	5	3	94	-110

H	K	L	FO	FC
14	5	-3	285	-298
17	5	3	103	111
17	5	-3	132	-195
20	5	3	100	-127
23	5	3	241	-269
3	6	3	2069	-2112
3	6	-3	706	635
6	6	3	1124	1063
6	6	-3	536	512
9	6	3	180	89
9	6	-3	1230	-1200
12	6	3	518	484
12	6	-3	659	625
15	6	3	271	188
18	6	3	450	468
18	6	-3	338	320
21	6	3	188	-174
1	7	3	403	-361
1	7	-3	565	-486
4	7	-3	1018	-1067
4	7	3	748	-732
7	7	3	580	580
7	7	-3	489	-522
10	7	3	262	232
10	7	-3	786	787
13	7	-3	106	84
16	7	3	194	-175
16	7	-3	489	-533
19	7	3	341	-348
19	7	-3	291	264
22	7	3	168	172
2	8	3	1448	1488
2	8	-3	336	366
5	8	3	1051	-1090
5	8	-3	577	-508
8	8	-3	718	710
11	8	3	656	-642
11	8	-3	739	-696
14	8	3	159	179
14	8	-3	200	209
17	8	3	94	-99
17	8	-3	224	-197
20	8	3	271	289
3	9	3	300	361
3	9	-3	341	-307
6	9	3	515	-495
6	9	-3	274	299
9	9	3	233	-270
9	9	-3	536	-562
12	9	3	127	-117
12	9	-3	106	198
15	9	3	127	98
15	9	-3	324	329
18	9	3	168	131
21	9	3	303	-315
1	10	3	762	-782
1	10	-3	150	-85
4	10	3	277	-266
4	10	-3	1277	1272
7	10	3	221	-238
7	10	-3	159	-161
10	10	3	768	772
10	10	-3	215	44
13	10	3	612	-566
13	10	-3	132	33
16	10	-3	203	229
19	10	3	103	114
19	10	-3	312	-329
2	11	3	303	296
2	11	-3	1160	-1166
5	11	3	674	714
5	11	-3	809	-754
8	11	3	315	-299
8	11	-3	830	836
11	11	3	97	114
11	11	-3	177	-172
14	11	-3	642	-669
17	11	3	118	-116
17	11	-3	106	-67
3	12	3	700	711
3	12	-3	821	848
6	12	3	862	846
6	12	-3	127	124
9	12	3	768	-690
9	12	-3	144	-147
12	12	3	621	551
12	12	-3	394	395
15	12	3	82	59
15	12	-3	94	35
18	12	-3	127	197
1	13	3	465	-477
1	13	-3	127	-154
4	13	3	500	-564
4	13	-3	989	-991
7	13	3	833	-821
7	13	-3	115	-93
10	13	-3	265	-259
13	13	3	91	109
13	13	-3	138	-126
16	13	3	144	-186

H	K	L	FO	FC
16	13	-3	68	71
2	14	3	191	-186
2	14	-3	1030	1022
5	14	3	233	228
5	14	-3	191	153
8	14	3	1195	1149
8	14	-3	615	600
11	14	3	474	-443
11	14	-3	185	192
14	14	3	77	6
14	14	-3	233	234
3	15	3	362	-349
3	15	-3	77	-107
6	15	3	421	-392
6	15	-3	374	-380
9	15	3	486	-456
9	15	-3	138	-129
12	15	3	94	-43
12	15	-3	159	-200
15	15	-3	285	-320
1	16	3	144	184
1	16	-3	106	-97
4	16	3	827	791
4	16	-3	244	230
7	16	3	177	127
7	16	-3	562	-580
10	16	3	241	252
10	16	-3	336	325
13	16	-3	180	195
2	17	3	159	-174
2	17	-3	609	-577
5	17	3	132	-151
8	17	3	115	-6
11	17	3	74	-35
11	17	-3	162	-182
	18	3	321	-331
6	18	3	127	76
6	18	-3	568	561
9	18	-3	250	-238
1	19	3	315	363
1	19	-3	235	201
4	19	3	262	-232
4	19	-3	100	17
7	19	3	265	-257
7	19	-3	118	105
10	19	3	159	132
2	20	3	153	130
2	20	-3	206	180
5	20	3	250	245
5	20	-3	556	-580
8	20	-3	194	217
3	21	3	112	112
1	22	3	188	-205
1	22	-3	118	-98
4	22	3	112	-87
2	23	3	235	-290
0	24	3	215	197
1	25	-3	50	-118
1	0	4	368	259
2	0	-4	1734	1828
4	0	4	1060	983
5	0	-4	492	514
8	0	-4	2202	2382
10	0	4	1292	1298
11	0	-4	397	-403
13	0	4	809	-799
14	0	-4	609	601
17	0	-4	539	496
20	0	-4	415	415
22	0	4	318	307
23	0	-4	71	-95
2	1	4	1613	-1503
3	1	-4	447	-323
5	1	4	977	-882
6	1	-4	1195	-1282
8	1	4	356	323
9	1	-4	977	-960
11	1	4	809	-809
12	1	-4	948	-936
14	1	4	112	-59
15	1	-4	250	292
17	1	4	297	310
20	1	4	288	-285
21	1	-4	330	-323
1	2	-4	1177	-1106
3	2	4	1533	1524
4	2	-4	553	490
6	2	4	221	193
7	2	-4	380	285
9	2	4	671	-623
10	2	-4	1083	1080
12	2	4	1192	1251
13	2	-4	241	-320
15	2	4	97	73
16	2	-4	703	701
21	2	4	415	-434
22	2	-4	274	290
24	2	4	333	367
1	3	4	1495	-1469
2	3	-4	403	323

H	K	L	FO	FC
4	3	4	1348	-1237
5	3	-4	877	-724
7	3	4	341	-315
8	3	-4	1048	-994
10	3	4	391	343
11	3	-4	547	528
13	3	4	924	-903
14	3	-4	653	-658
16	3	4	389	-429
17	3	-4	553	-552
19	3	4	306	269
22	3	4	165	-174
2	4	4	1757	1749
3	4	-4	977	818
5	4	4	138	103
6	4	-4	480	427
8	4	4	674	663
9	4	-4	1110	-1162
11	4	4	135	127
12	4	-4	356	341
14	4	4	418	435
15	4	-4	153	-162
17	4	4	177	189
18	4	-4	477	481
20	4	4	586	611
21	4	-4	127	-127
23	4	4	174	-191
1	5	-4	336	-254
3	5	4	1062	-1046
6	5	4	483	-442
6	-5	-4	1236	-882
7	5	-4	253	235
9	5	4	474	-431
10	5	-4	112	179
15	5	4	79	-20
18	5	4	253	-213
21	5	4	303	-300
1	6	4	1442	-1515
2	6	-4	571	-526
4	6	4	1598	1700
5	6	-4	124	118
7	6	4	277	-271
8	6	-4	815	904
10	6	4	406	369
11	6	-4	771	-827
13	6	4	315	321
14	6	-4	500	556
16	6	4	218	268
17	6	-4	318	-298
19	6	4	100	-79
20	6	-4	118	134
22	6	4	347	331
2	7	4	380	-311
3	7	-4	215	176
5	7	4	954	948
6	7	-4	109	94
8	7	4	698	-670
9	7	-4	215	152
11	7	4	795	-817
12	7	-4	165	201
14	7	4	156	-159
15	7	-4	62	-99
18	7	-4	74	-55
21	7	-4	88	152
1	8	-4	318	-285
3	8	4	1171	-1131
4	8	-4	957	918
6	8	4	218	-118
7	8	-4	583	-555
10	8	-4	100	29
12	8	4	512	462
13	8	-4	118	135
15	8	4	330	-317
16	8	-4	235	228
18	8	4	82	82
19	8	-4	353	-403
1	9	4	656	654
2	9	-4	1469	-1481
4	9	4	483	-471
5	9	-4	421	-402
7	9	4	280	301
8	9	-4	518	517
11	9	-4	474	-489
13	9	4	182	-165
14	9	-4	253	-258
16	9	4	141	131
17	9	-4	197	199
19	9	4	209	-235
2	10	4	907	864
3	10	-4	238	232
5	10	4	424	401
6	10	-4	562	559
8	10	4	806	781
9	10	-4	168	193
12	10	-4	197	173
14	10	4	194	203
15	10	-4	79	1
17	10	4	65	47
18	10	-4	138	210
1	11	-4	303	-237

Table 4 (*cont.*)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	11	4	327	300	8	18	-4	336	364	4	3	-5	203	192	10	8	6	477	462	13	15	-5	53	-49
4	11	-4	327	-285	10	18	4	106	132	5	3	5	1189	-1141	13	8	5	389	-344	2	16	-5	235	226
6	11	4	380	-333	2	19	4	88	-168	7	3	-5	951	-859	16	8	5	147	134	3	16	5	191	-143
7	11	-4	842	-858	3	19	-4	330	349	8	3	5	212	-181	18	8	-5	74	113	5	16	-5	79	-125
9	11	4	203	-166	5	19	4	77	72	10	3	-5	253	-282	1	9	-5	474	-408	6	16	5	439	369
10	11	-4	188	-160	6	19	-4	97	70	11	3	5	883	-865	2	9	5	280	-324	8	16	-5	353	427
12	11	4	253	239	8	19	4	71	86	13	3	-5	233	191	4	9	-5	736	-695	9	16	5	103	104
15	11	4	74	38	1	20	-4	109	115	14	3	5	271	-366	5	9	5	783	753	12	16	5	59	93
16	11	-4	82	-149	3	20	4	168	113	16	3	-5	141	-229	7	9	-5	409	-406	1	17	5	406	-386
18	11	4	79	93	4	20	-4	274	320	17	3	5	389	371	8	9	5	256	306	3	17	-5	153	109
1	12	4	456	-414	6	20	4	88	-99	19	3	-5	115	-228	10	9	-5	627	670	4	17	5	277	-265
2	12	-4	1598	1753	7	20	-4	159	-168	20	3	5	127	-126	11	9	5	115	-61	7	17	5	156	-121
4	12	4	221	-187	2	21	-4	182	-193	2	4	-5	403	-389	13	9	-5	218	-258	9	17	-5	118	109
5	12	-4	180	-66	4	21	4	206	-201	3	4	5	350	-345	14	9	5	124	116	1	18	-5	218	216
7	12	4	283	-319	5	21	-4	132	-158	5	4	-5	177	86	16	9	-5	215	-241	2	18	5	285	266
8	12	-4	327	355	7	21	4	150	-190	6	4	5	1036	967	17	9	5	71	-84	4	18	-5	79	-25
10	12	4	783	759	2	22	4	71	-45	8	4	-5	571	543	2	10	-5	1207	1142	5	18	5	247	213
11	12	-4	235	223	3	22	-4	162	-179	9	4	5	333	318	3	10	5	336	-290	7	18	-5	312	-338
13	12	4	374	-361	5	22	4	135	106	11	4	-5	439	-432	5	10	-5	492	-500	8	18	5	85	151
14	12	-4	203	186	6	22	-4	38	110	12	4	5	589	549	6	10	5	218	-153	10	18	-5	94	127
16	12	4	77	-102	2	24	-4	91	131	14	4	-5	386	398	8	10	-5	253	217	2	19	-5	79	-12
17	12	-4	91	-195	1	0	-5	512	-497	15	4	5	265	303	9	10	5	574	-590	3	19	5	115	161
2	13	4	159	195	2	0	5	786	779	17	4	-5	135	-165	11	10	-5	130	102	6	19	5	79	-90
3	13	-4	751	-806	4	0	-5	1077	1035	18	4	5	353	352	12	10	5	559	565	8	19	-5	47	-96
5	13	4	244	-277	5	0	5	742	719	20	4	-5	250	256	14	10	-5	150	198	1	20	5	300	-345
6	13	-4	94	6	7	0	-5	79	38	21	4	5	215	-242	17	10	-5	109	-142	3	20	-5	130	-183
8	13	4	415	-427	8	0	5	742	685	1	5	5	1174	-1076	18	10	5	47	-74	4	20	5	265	-198
9	13	-4	112	-79	10	0	-5	1221	1190	3	5	-5	494	-377	1	11	5	383	-311	6	20	-5	233	269
12	13	-4	542	-569	11	0	5	986	-989	4	5	5	494	-523	3	11	-5	177	-128	1	21	-5	74	106
14	13	4	68	-34	13	0	-5	147	-69	6	5	-5	150	-159	4	11	5	365	-373	2	21	5	82	40
15	13	-4	191	-166	14	0	5	983	944	9	5	-5	336	331	6	11	-5	150	198	5	21	5	118	-112
1	14	-4	218	-187	16	0	-5	497	457	10	5	5	124	-4	9	11	-5	580	-549	2	22	-5	118	114
4	14	-4	668	640	20	0	5	191	-145	12	5	-5	415	-385	10	11	5	88	-27	3	22	5	185	161
6	14	4	639	647	23	0	5	124	-160	13	5	5	677	-653	12	11	-5	374	-372	1	24	-5	182	-178
7	14	-4	394	-426	2	1	-5	153	183	15	5	-5	197	-204	15	11	-5	156	183	0	0	6	362	390
9	14	4	271	-271	3	1	5	1898	-1978	16	5	5	303	-366	4	12	-5	803	782	0	3	-6	206	273
10	14	-4	406	429	5	1	-5	703	-679	18	5	-5	82	25	5	12	5	383	-332	0	6	6	1271	1327
12	14	4	177	173	6	1	5	200	-248	1	6	-5	621	473	7	12	-5	244	-263	0	6	-6	397	383
13	14	-4	244	284	8	1	-5	185	-137	2	6	5	1554	1641	8	12	5	845	818	0	9	6	603	-597
15	14	4	82	68	9	1	5	259	165	5	6	5	391	-323	10	12	-5	486	495	0	9	-6	974	-1037
1	15	4	733	-721	11	1	-5	471	456	7	6	-5	574	-569	11	12	5	447	-467	0	12	6	700	661
2	15	-4	450	-465	12	1	5	91	-150	8	6	5	347	-318	13	12	-5	141	164	0	12	-6	1001	1028
4	15	4	212	201	14	1	-5	1074	-1085	10	6	-5	200	182	14	12	5	82	-154	0	18	6	468	449
5	15	-4	288	299	15	1	5	430	-448	11	6	5	144	111	16	12	-5	53	84	0	18	-6	285	-292
7	15	4	156	-139	17	1	-5	394	-358	14	6	5	371	354	2	13	-5	1004	-1043	0	21	-6	165	-212
8	15	-4	127	-75	18	1	5	330	-309	16	6	-5	303	323	6	13	5	300	-252	0	4	-7	786	790
10	15	4	71	-127	20	1	-5	91	180	17	6	5	203	-190	8	13	-5	103	-78	0	7	-7	465	-458
11	15	-4	74	-75	21	1	5	94	-10	19	6	-5	391	-422	9	13	5	218	-241	0	8	7	609	639
3	16	-4	59	-54	23	1	-5	150	-163	20	6	5	256	303	11	13	-5	144	-155	0	10	-7	648	628
5	16	4	124	-130	1	2	5	441	435	2	7	-5	515	-456	12	13	5	100	38	0	11	7	288	-285
6	16	-4	327	338	3	2	-5	539	-528	3	7	5	200	215	14	13	-5	153	-189	0	13	-7	303	-454
8	16	4	550	560	4	2	5	1848	1847	5	7	-5	362	337	1	14	5	91	107	0	14	7	612	610
9	16	-4	244	-231	6	2	-5	871	884	6	7	5	341	-341	4	14	5	536	481	0	20	7	127	185
12	16	-4	150	165	7	2	5	683	-599	8	7	-5	344	366	6	14	-5	227	315	0	4	8	494	499
1	17	-4	79	47	9	2	-5	597	-598	9	7	5	439	-405	7	14	5	109	-125	0	8	-8	315	349
3	17	4	94	-149	10	2	5	668	591	11	7	-5	191	-221	9	14	-5	174	-100	0	10	8	356	367
4	17	-4	103	-150	12	2	-5	936	986	15	7	5	121	-97	10	14	5	492	507	0	11	-8	489	-542
6	17	4	409	-387	13	2	5	227	223	17	7	-5	162	183	12	14	-5	227	255	0	14	-8	138	239
7	17	-4	247	207	15	2	-5	371	370	18	7	5	62	-38	13	14	5	77	-36	0	16	8	403	450
9	17	4	218	-267	16	2	5	268	260	1	8	5	1404	-1306	2	15	5	138	99	0	3	-9	262	-286
10	17	-4	77	-128	18	2	-5	609	561	3	8	-5	648	571	4	15	-5	191	-238	0	6	9	215	227
1	18	4	656	-640	19	2	5	191	-188	4	8	5	592	598	5	15	5	135	-87	0	6	-9	368	479
2	18	-4	177	-171	21	2	-5	68	-86	6	8	-5	633	590	8	15	5	386	-394	0	12	9	212	283
4	18	4	253	274	22	2	5	303	327	7	8	5	371	315	10	15	-5	300	-332	0	12	-9	180	206
5	18	-4	674	-690	1	3	-5	162	-118	9	8	-5	468	-473	11	15	5	115	-90	0	4	-10	177	212
7	18	4	238	236	2	3	5	177	180															

their thermal parameters, with their e.s.d.'s, in Table 2; the positional parameters of hydrogen atoms, calculated on the final positions of carbon atoms, and their assumed isotropic temperature factors in Table 3; the observed and calculated structure factors in Table 4. The peak heights and curvatures for non-hydrogen atoms, and their e.s.d.'s, obtained from differential synthesis, are given in Table 5.

Three cycles of anisotropic least-squares refinement were also carried out with the use of 1213 reflexions, which were less affected by, and were not corrected for, secondary extinction. These reflexions were selected by taking the reflexions nearer to the origin of the plot of log F_o/F_c *versus* I_c on the left side of the vertical lines indicated on the diagrams of Fig. 1. A final value of $R=0{\cdot}087$ was obtained. The bond distances and angles corresponding to this refinement are given in Table 8 for comparison with those obtained from the 1327 reflexions corrected for secondary extinction. Similarly the other functions calculated for this refinement with the 1213 uncorrected reflexions do not differ significantly from those obtained from the 1327 corrected reflexions and are therefore omitted from the text.

Computing methods

The following calculations were performed on an IBM 1620 (20 K) computer at the Centro di Calcolo elettronico dell'Università di Modena:

(i) Intensity corrections; structure factor calculations; Patterson, F_o and F_o–F_c syntheses with the programs of Scatturin and co-workers (Albano, Bellon & Pompa, 1963; Pompa, Albano, Bellon & Scatturin, 1963) and of King and Van der Helm (King & Van der Helm, 1963; King, 1964).

(ii) Isotropic least-squares refinement with the program of D. Van der Helm revised to card by C. N. Caughlan and G. W. Svetich (Chemistry Department, Montana State College), using 3 × 3 matrices for the positional parameters and 1 × 1 matrices for the isotropic temperature factor parameters of each atom.

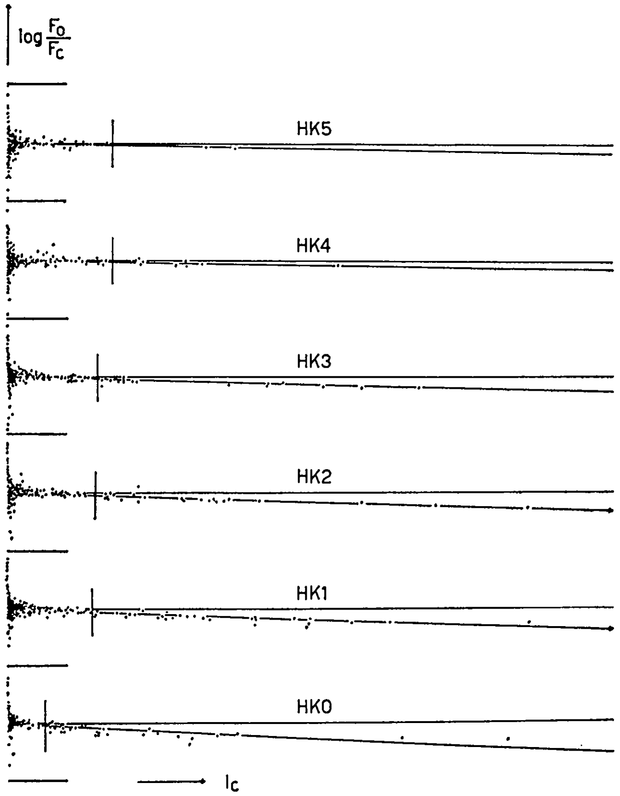


Fig. 1. Plot of $\log (F_o/F_c)$ *versus* I_c showing the decrease of secondary extinction for the succecive *hkl* layers from $l=0$ to $l=5$.

(iii) Differential Fourier syntheses with the program of E. Giglio, A. Ripamonti and co-workers (Damiani, De Santis, Giglio & Ripamonti, 1963).

Special modifications to the programs used and various minor programs were written in this Institute and in the Centro di Calcolo elettronico dell'Università di Modena.

The final anisotropic refinement was performed on an IBM 7094 computer with the full-matrix ORFLS program of Busing and co-workers (Busing, Martin & Levy, 1962). R.M.S. components of atomic thermal displacement and their orientations, bond lengths and angles and their e.s.d.'s, angles between normals to planes, and other functions, were calculated on the IBM 7094 computer with the ORFEE program of Busing and co-workers (Busing, Martin & Levy, 1964).

Results and discussion

Molecular structure

The nickel atom lies at a centre of symmetry, being planar-bonded to four sulphur atoms of two dithiocarbamic ligands. The numbering of non-hydrogen atoms is given in Fig. 4(*a*), representing, in projection on the X–Y plane, the asymmetric unit used for the calculation.

Hydrogen atoms were identified in their calculated positions from a three-dimensional difference Fourier synthesis, using structure factors calculated only with non-hydrogen atoms.

The composite drawing of Fig. 2 shows the three-dimensional sections of the residual electron density,

Table 5. *Peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5}) *from differential synthesis, and their e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
Ni	obs.	37·01	314·2	329·4	210·7	157·6	0·0	9·1
	calc.	37·15	317·4	331·6	214·2	158·4	−0·1	9·2
S(1)	obs.	22·07	202·6	198·7	115·2	98·0	−5·8	6·6
	calc.	22·15	202·9	198·8	116·6	97·6	−6·0	6·5
S(2)	obs.	22·43	197·4	210·3	111·0	97·6	−10·5	9·1
	calc.	22·49	198·0	211·1	111·8	98·0	−10·0	8·9
N	obs.	8·28	61·7	67·4	39·4	32·9	−1·8	0·2
	calc.	8·24	62·7	69·3	40·2	33·7	−1·8	0·6
C(0)	obs.	6·26	45·3	52·5	32·7	23·0	−1·6	−2·0
	calc.	6·20	46·1	53·6	34·4	23·2	−1·3	−2·3
C(1)	obs.	5·90	38·2	45·6	31·2	20·3	−2·5	2·5
	calc.	5·91	39·4	46·1	31·0	20·8	−2·6	2·2
C(2)	obs.	5·23	31·6	32·9	22·7	18·0	2·7	−0·6
	calc.	5·21	30·5	31·2	22·1	16·7	2·7	0·2
C(3)	obs.	3·97	25·6	23·2	14·4	15·3	0·1	−1·9
	calc.	4·03	25·5	22·4	14·0	14·4	0·5	−2·5
C(4)	obs.	6·12	45·0	45·0	35·9	21·9	−0·9	−1·6
	calc.	6·15	46·1	46·0	37·0	22·4	−1·2	−1·7
C(5)	obs.	5·87	41·8	42·1	28·0	21·7	−3·9	−0·8
	calc.	5·86	41·5	41·3	28·3	21·5	−3·4	−0·9
C(6)	obs.	4·95	31·2	34·1	23·5	15·0	0·3	−0·1
	calc.	5·01	32·4	34·2	24·1	14·7	1·0	−0·4
		$\sigma(\varrho)$	$\sigma(A_{hh})$	$\sigma(A_{kk})$	$\sigma(A_{ll})$	$\sigma(A_{hk})$	$\sigma(A_{hl})$	$\sigma(A_{kl})$
		0·11	1·94	1·94	1·21	1·37	0·94	0·93

projected on the X–Y plane. In the numbering of hydrogen atoms the first number is that of the corresponding carbon atom. It may be observed that all hydrogen atoms of the CH_2 group are fairly well centred on the calculated positions, while the hydrogen atoms H(31), H(32), H(33), H(61), H(62) and H(63) are out of their calculated centres.

Also the electron densities at the calculated positions of hydrogen atoms (Table 6), obtained from final F_o and F_c values, show that the hydrogen atoms of the CH_2 groups have ϱ_o–ϱ_c differences whose mean value is within the value of $\sigma(\varrho)=0{\cdot}11$ e.Å^{-3} calculated for the whole structure. The hydrogen atoms of the CH_3 groups on the other hand have a mean ϱ_o–ϱ_c value

Table 6. *Electron densities*, ϱ_o, ϱ_c *and* ϱ_o–ϱ_c (e.Å^{-3}) *at the calculated positions of hydrogen atoms*

	ϱ_o	ϱ_c	$\varrho_o-\varrho_c$		ϱ_o	ϱ_c	$\varrho_o-\varrho_c$
H(11)	0·45	0·43	+0·02	H(31)	0·44	0·86	−0·42
H(12)	1·01	1·07	−0·06	H(32)	0·47	0·71	−0·24
H(21)	1·32	1·47	−0·15	H(33)	1·00	1·26	−0·26
H(22)	0·63	0·81	−0·18	H(61)	0·68	0·45	+0·23
H(41)	0·77	0·87	−0·10	H(62)	0·59	0·81	−0·22
H(42)	0·82	0·86	−0·04	H(63)	0·51	0·77	−0·26
H(51)	0·82	0·89	−0·07				
H(52)	0·48	0·62	−0·14				
	Mean value 0·10				Mean value 0·27		

Table 7. *R.M.S. components of atomic thermal displacement* (Å) *along the thermal ellipsoid principal axes and their e.s.d.'s, and orientations of the ellipsoid principal axes with respect to the crystal axial vectors* **a**, **b**, **c** *and to the vector* Ni→C(0)

	Principal axis	R.M.S. displacement	Angle (°) to reference axis			
			a	**b**	**c**	Ni → C(0)
Ni	1	0·212 (3) Å	42 (6)	73 (4)	131 (6)	146 (6)
	2	0·231 (3)	129 (8)	96 (17)	138 (7)	56 (6)
	3	0·238 (2)	77 (11)	19 (7)	83 (14)	87 (10)
S(1)	1	0·229 (3)	48 (17)	98 (18)	120 (4)	148 (16)
	2	0·235 (3)	133 (18)	165 (11)	96 (9)	63 (18)
	3	0·275 (3)	73 (3)	102 (3)	30 (3)	106 (3)
S(2)	1	0·221 (3)	39 (11)	82 (8)	124 (8)	153 (10)
	2	0·233 (3)	128 (11)	141 (4)	125 (7)	68 (11)
	3	0·262 (3)	98 (3)	52 (4)	127 (4)	76 (3)
N	1	0·208 (9)	46 (16)	93 (9)	123 (17)	149 (17)
	2	0·233 (9)	130 (16)	113 (14)	139 (16)	60 (17)
	3	0·261 (8)	72 (10)	23 (14)	111 (13)	97 (9)
C(0)	1	0·193 (14)	102 (18)	74 (9)	151 (14)	79 (19)
	2	0·220 (10)	158 (13)	107 (12)	71 (18)	11 (19)
	3	0·261 (10)	72 (10)	24 (10)	69 (8)	91 (10)
C(1)	1	0·209 (11)	48 (8)	99 (6)	119 (12)	148 (9)
	2	0·255 (13)	111 (15)	84 (18)	151 (12)	72 (13)
	3	0·284 (10)	50 (9)	10 (10)	89 (16)	116 (8)
C(2)	1	0·264 (12)	48 (11)	108 (11)	93 (11)	147 (11)
	2	0·316 (12)	135 (43)	157 (79)	75 (27)	57 (14)
	3	0·320 (15)	77 (92)	76 (21)	16 (25)	93 (70)
C(3)	1	0·258 (13)	109 (7)	49 (7)	89 (6)	56 (7)
	2	0·331 (14)	149 (10)	133 (9)	116 (12)	46 (10)
	3	0·387 (16)	114 (11)	110 (9)	26 (12)	62 (10)
C(4)	1	0·208 (15)	89 (40)	79 (23)	12 (9)	80 (39)
	2	0·220 (9)	178 (22)	121 (13)	89 (39)	17 (25)
	3	0·271 (10)	91 (8)	33 (8)	102 (9)	76 (9)
C(5)	1	0·241 (14)	78 (18)	63 (53)	27 (46)	89 (17)
	2	0·246 (10)	167 (12)	111 (61)	81 (6)	6 (41)
	3	0·270 (11)	86 (19)	35 (19)	115 (20)	84 (19)
C(6)	1	0·234 (10)	20 (15)	47 (11)	104 (25)	151 (7)
	2	0·256 (14)	101 (24)	105 (19)	165 (22)	89 (23)
	3	0·304 (11)	106 (7)	47 (7)	97 (11)	61 (7)

more than twice that of the $\sigma(\varrho)$ value. It may be assumed that the positions of the CH_2 hydrogen atoms are sufficiently reliable for their intermolecular distances to be considered significant.

The greater displacement from the calculated positions of the hydrogen atoms of the CH_3 groups may be due to the greater anisotropic motion and to the possibility of free rotation of the terminal methyl groups. This is specially true for the C(3) group which lies on the surface of a vertical CH_3 channel (Fig. 5) in which hydrogen atoms of neighbouring groups can interfere sterically each other.

R.M.S. components of atomic thermal displacement in Å (with their e.s.d.'s) along the ellipsoid principal axes $1<2<3$ and the orientations of the ellipsoid principal axes with respect to the crystal axial vectors **a**, **b**, **c**, and to the vector $Ni\rightarrow C(0)$ were calculated with the ORFEE program (Busing, Martin & Levy, 1964) (Table 7). The projection of the thermal ellipsoids along an axis normal to Y axis and making an angle of about $-55°$ with the $X-Y$ plane is shown in Fig. 3. The maximum thermal displacement of the C(3) atom is in a direction close to the c axis, that is to the axis of the CH_3 channel indicated by a circle in Fig. 5. The direction of maximum thermal displacement for the atoms C(4), C(5), C(6) is almost normal to their plane.

Bond lengths and angles (with their e.s.d.'s) were calculated with the ORFEE program (Busing, Martin & Levy, 1964). Table 8 shows the comparison of the set of values obtained from 1213 reflexions less affected by and uncorrected for secondary extinction with the set of values obtained from 1327 reflexions corrected for secondary extinction. It may be remarked that the e.s.d. values calculated with the ORFEE program may perhaps be a little optimistic. The greater differences between the two series of values are on the carbon–carbon distances. Their positions are more sensitive to the 114 reflexions which were excluded from the first set of 1213 reflexions as they are more affected by secondary extinction and have lower $\sin\theta/\lambda$ values.

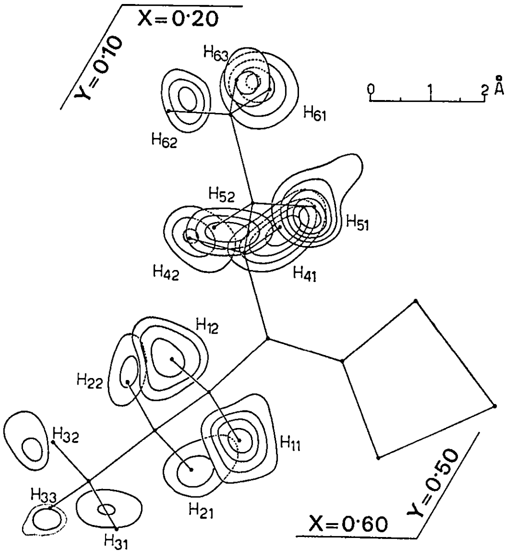


Fig. 2. Sections of the difference electron density map, projected on the $X-Y$ plane, corresponding to the calculated positions for hydrogen atoms. Contours are at 0·1 e.Å^{-3} intervals, beginning with the 0·15 e.Å^{-3} contour.

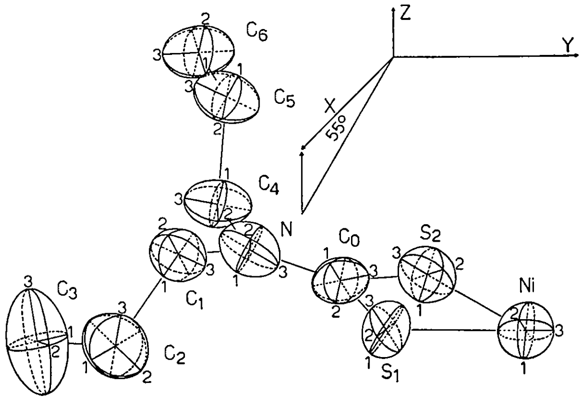


Fig. 3. Projection of the thermal ellipsoids along an axis normal to Y and making an angle of about 55° with the $X-Y$ plane. 1,2,3 are the principal axes of the ellipsoid in the order: minimum, medium, maximum.

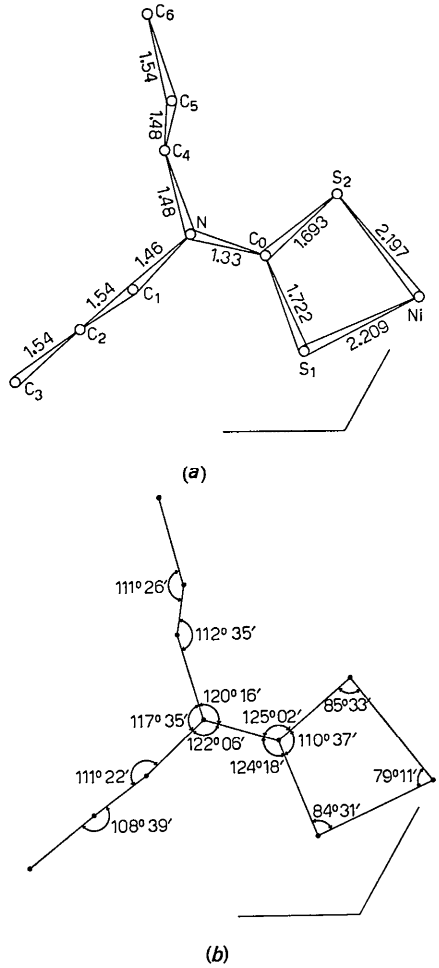


Fig. 4. (a) Bond distances (Å) and (b) angles for the asymmetric unit.

Table 8. *Bond lengths and angles and their e.s.d.'s*

(*A*) Values obtained from least-squares refinement of 1213 reflexions without secondary extinction correction. $R=0.087$.

(*B*) Values obtained from least-squares refinement of 1327 reflexions corrected for secondary extinction. $R=0.075$.

	(*A*)		(*B*)	
Ni —S(1)	2·210	± 0·002 Å	2·209	± 0·002 Å
Ni —S(2)	2·199	0·002	2·197	0·002
S(1)–C(0)	1·726	0·008	1·722	0·008
S(2)–C(0)	1·702	0·008	1·693	0·008
N—C(0)	1·33	0·009	1·33	0·009
N—C(1)	1·47	0·010	1·46	0·010
N—C(4)	1·48	0·010	1·48	0·010
C(1)–C(2)	1·56	0·014	1·54	0·013
C(2)–C(3)	1·55	0·015	1·54	0·014
C(4)–C(5)	1·51	0·013	1·48	0·012
C(5)–C(6)	1·52	0·013	1·54	0·012

	(*A*)		(*B*)	
S(1)–Ni —S(2)	79° 23′	± 05′	79° 11′	± 05′
Ni —S(1)–C(0)	84 36	16	84 31	16
Ni —S(2)–C(0)	85 28	16	85 33	16
S(1)–C(0)–S(2)	110 27	25	110 37	25
S(1)–C(0)–N	124 34	39	124 18	37
S(2)–C(0)–N	124 54	38	125 02	37
C(0)–N—C(1)	121 48	42	122 06	41
C(0)–N—C(4)	120 00	41	120 16	39
C(1)–N—C(4)	118 08	38	117 35	37
N—C(1)–C(2)	110 10	44	111 22	46
C(1)–C(2)–C(3)	107 10	56	108 39	56
N—C(4)–C(5)	112 14	41	112 35	41
C(4)–C(5)–C(6)	110 31	46	111 26	45

In the following discussion only the bond lengths and angles obtained from the 1327 reflexions, corrected for secondary extinction, will be considered.

The Ni–S distances (2·209 and 2·197 Å), in very good agreement with those (2·207 and 2·195 Å) obtained for nickel(II) bis(*N*,*N*-diethyldithiocarbamate) (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), lie in the range 2·1–2·3 Å now accepted for Ni–S bonds in four planar coordinated diamagnetic complexes of nickel: *e.g.* 2·16 Å in bisthiosemicarbazidato-nickel(II) (Cavalca, Nardelli & Fava, 1962); 2·23, 2·24 Å in nickel xanthate (Franzini, 1963).

The S–C distances (1·722 and 1·693 Å) are close to those (1·713 and 1·700 Å) obtained for nickel(II) bis-(*N*,*N*-diethyldithiocarbamate); their average value, S–C 1·71 Å, seems to be normal for a S–C(sp^2) bond.

The S(1)–Ni–S(2) angle (79° 11′) corresponds to a distortion from exact square planar coordination with dsp^2 hybridization of the valence orbitals of the nickel atom, due to the strain in the four-membered ring. In both dipropyl- and diethyl-dithiocarbamates the four membered rings show a dissymmetry between the two Ni–S and the two C(0)–S bonds; their differences are:

	Propyl derivative	Ethyl derivative
Ni–S(1) > Ni–S(2)	0·012 Å	0·012 Å
C(0)–S(1) > C(0)–S(2)	0·029	0·013

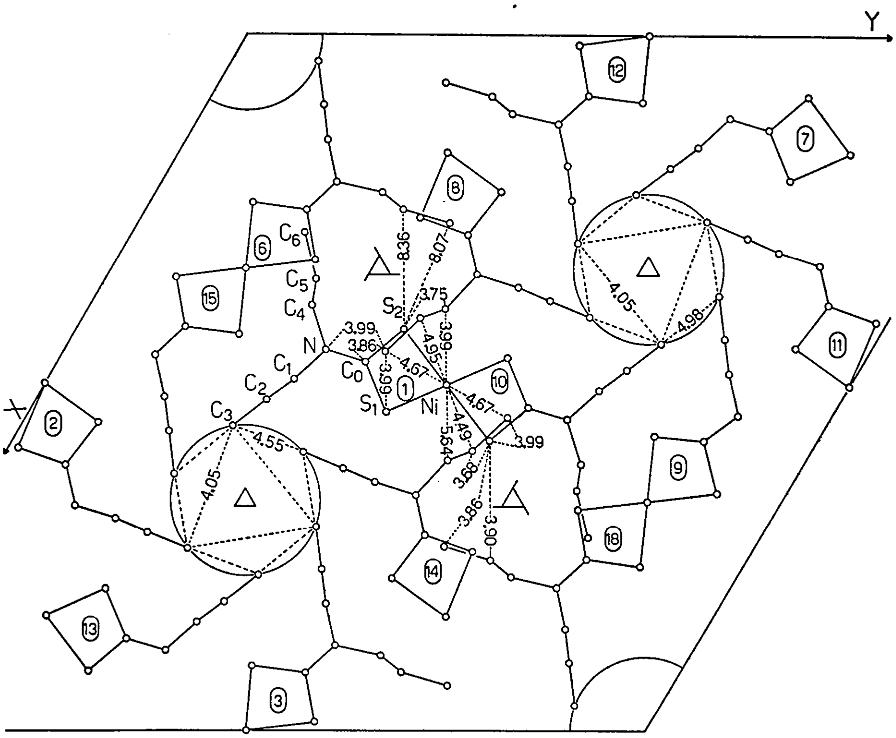
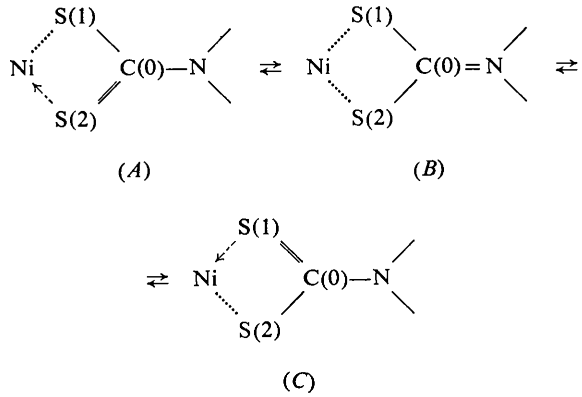


Fig. 5. Projection of part of the crystal structure on the $X-Y$ plane, showing the environment of the central molecule and the principal intermolecular distances. Asymmetric units are indicated by their order number inscribed in an O.

These differences could be considered significant in admitting a different contribution of the two forms, (*A*) slightly greater than (*C*):



The N–C(0) bond (1·33 Å), as in nickel diethyldithiocarbamate, shows a high double bond character. Its double bond order, in the LCAO-MO approximation, calculated by Coulson's formula for the C–C bond (Coulson, 1939), modified for the C–N bond by Liquori and Vaciago (Liquori & Vaciago, 1965; Favini, Mazzeo & Vaciago, 1963):

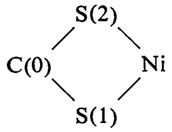
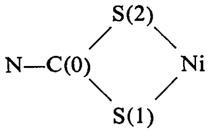
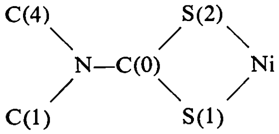
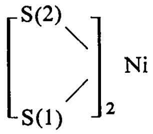
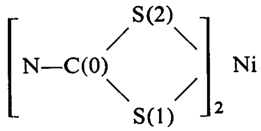
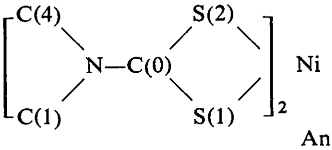
$$R=S-\frac{S-D}{1+0{\cdot}6625\,(1-p)/p}\qquad S=1{\cdot}475\ \text{Å}\qquad D=1{\cdot}280\ \text{Å}$$

is $p=0{\cdot}65$.

It is therefore confirmed that the (*B*) form, as already recognized by infrared spectroscopic work (Chatt, Duncanson & Venanzi, 1956*a*,*b*) is an important canonical form in the structure of dialkyldithiocarbamates, while the $\cdots S_2C=OR$ form makes only a minor contribution to the structure of xanthates (Chatt, Duncanson & Venanzi, 1956*a*,*b*) as is also shown by the longer C–O = 1·38 Å distance in nickel xanthate (Franzini, 1963).

The N–C(1) (1·46 Å) and N–C(4) (1·48 Å) bonds have an average value (1·47 Å) close to the value of 1·475 Å for a N–C single bond.

Table 9. *Coefficients* (×10³) *of the least-squares planes of the form* $x+By+Cz+D=0$ *and atom deviations from the planes*

	Plane	Plane coefficients (×10³)			Atom deviations (Å) from the plane						
		B	*C*	*D*	Ni	S(1)	S(2)	C(0)	N	C(1)	C(4)
(1)		442	2930	−23434	0·018	−0·023	−0·021	0·026	0·138	0·219	0·246
(2)		348	2700	−22049	0·057	−0·045	−0·033	−0·023	0·044	0·096	0·132
(3)		279	2591	−21355	0·091	−0·044	−0·046	−0·053	−0·017	0·022	0·047
(4)		518	3100	−24427	0	0	0	0·070	0·212	0·312	0·337
(5)		407	2804	−22791	0	−0·071	−0·054	−0·028	0·065	0·129	0·171
(6)		347	2703	−22229	0	−0·101	−0·092	−0·081	−0·013	0·039	0·073

Angle between: plane *X*−*Y* and plane (4) 19° 58′
plane *X*−*Y* and plane (5) 21 03
plane *X*−*Y* and plane (6) 21 23

Planarity of the molecule

The central part of the molecule is approximately planar as far as the C(1) and C(4) atoms. The deviations of the atoms of this central part of the molecule from six least-square planes are listed in Table 9. From the more general plane no. 6, which includes C(1) and C(4) atoms, the atoms have a maximum and mean deviation of 0·100 and 0·060 Å respectively.

Table 10 gives the angles between the normals to some planes of this central part of the molecule: the dihedral angle of the planes Ni–S(1)–S(2) ∧ N–C(4)–C(1) has a value of 8°29′ and the dihedral angles Ni–S(2)–S(1) ∧ C(0)–S(1)–S(2) ∧ N–C(4)–C(1) a value of about 4°; all other dihedral angles have values of about 3°.

Table 10. *Angles between normals to planes, each defined by three atoms* (1,2,3) *and* (4,5,6), *and their e.s.d.'s*

The direction of the normals is that of (1 → 2) × (1 → 3) and (4 → 5) × (4 → 6) where (1 → 2) is the vector defined by atoms 1 and 2 *etc.*

1,2,3	4,5,6		
Ni —S(2)–S(1)	N——C(4)–C(1)	8°29′	±0°43′
C(0)–S(2)–N	N——C(0)–C(4)	0 38	1 08
N——C(1)–C(0)	C(0)–N——S(1)	0 37	1 10
Ni —S(2)–S(1)	C(0)–S(1)–S(2)	4 06	0 30
C(0)–S(1)–S(2)	N——C(4)–C(1)	4 24	0 51
S(1)–Ni —C(0)	S(2)–C(0)–Ni	3 37	0 26
C(0)–N——S(1)	C(0)–S(2)–N	2 48	1 13
N——C(1)–C(0)	N——C(0)–C(4)	2 49	1 15
N——C(4)–C(1)	N——C(0)–C(4)	2 41	1 12
N——C(4)–C(1)	N——C(1)–C(0)	2 45	1 13
C(0)–S(1)–S(2)	C(0)–S(2)–N	2 28	1 05
C(0)–S(1)–S(2)	C(0)–N——S(1)	2 27	1 04

Intermolecular contacts

The environment of the central molecule with Ni in position ($\frac{1}{2},\frac{1}{2},0$) is represented in Fig. 5 with some intermolecular distances. In Figs. 5 and 6, in Table 11 and in the text the asymmetric units not related by a centre of symmetry are numbered 1 to 9 in the same sequence as in *International Tables for X-ray Crystallography* (1952) for the space group $R\bar{3}$ (no. 148), with hexagonal axes; the asymmetric units related to the units 1–9 by a centre of symmetry are numbered 10 to 18. An asymmetric unit belonging to the lower cell and corresponding to the one labelled in Fig. 5 is indicated by the same number with a prime.

Table 11. *Intermolecular distances shorter than* 4·0 Å, *from atoms of asymmetric unit* (1) *to atoms of asymmetric units* (6′), (8) *and* (8′)

Ni(−·1)—C(4·8)	3·99 Å
S(1·1)——C(6·8)	3·99
S(2·1)——C(4·8)	3·75
S(2·1)——C(5·8′)	3·68
S(2·1)——C(6·8′)	3·99
S(2·1)——C(5·6′)	3·90
S(2·1)——C(6·6′)	3·86
C(0·1)——C(6·8)	3·86
N(−·1) —C(6·8)	3·99

Three methyl groups are coplanar around the trigonal axis at a van der Waals distance C–C of 4·05 Å. Each methyl group has C–C distances of 4·55 Å from the nearest methyl group of the plane above, and of 4·98 Å from the nearest methyl group of the plane below. These distances may explain the greater free-

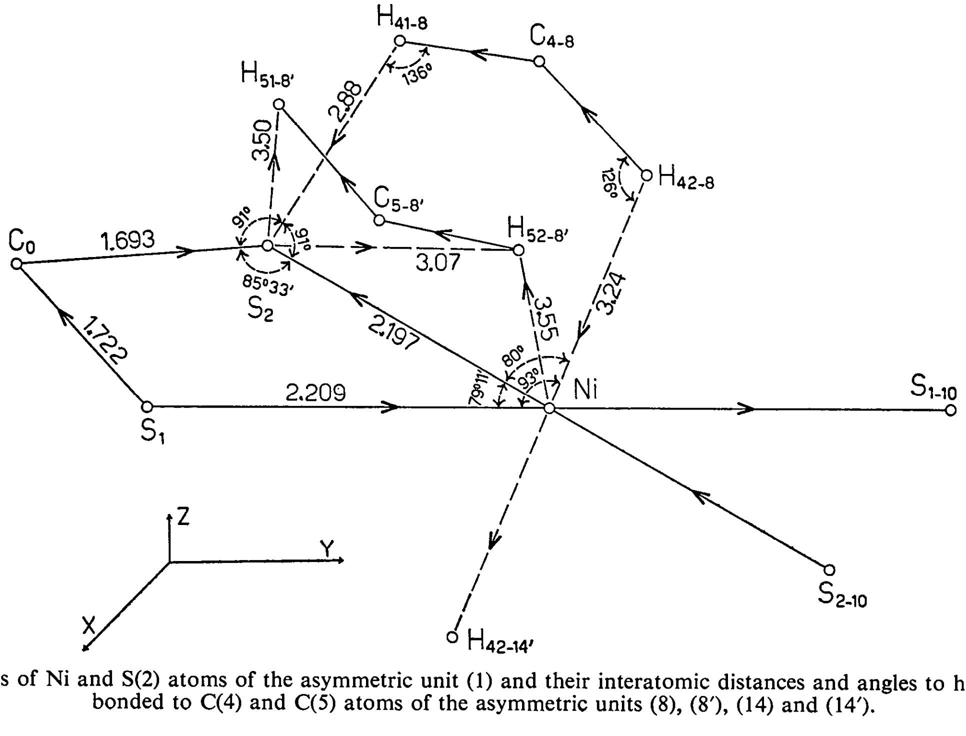


Fig. 6. Contacts of Ni and S(2) atoms of the asymmetric unit (1) and their interatomic distances and angles to hydrogen atoms bonded to C(4) and C(5) atoms of the asymmetric units (8), (8′), (14) and (14′).

dom of thermal motion observed for the C(3) atom approximately along the trigonal axis, which is the axis of the channel formed by superposition of successive planes of three methyl groups.

The intermolecular distances, between non-hydrogen atoms, shorter than 4·0 Å, are listed in Table 11 and Fig. 5. It has already been shown that the CH_2 hydrogen atom positions may be sufficiently reliable; the distances and angles of the intermolecular contacts between Ni and S(2) atoms of the asymmetric unit 1 and the hydrogen atoms H(41), H(42) of the asymmetric unit 8 and H(51), H(52) of the asymmetric unit 8′ are therefore given in Fig. 6.

The S(2)–H(41–8) distance (2·88 Å) is shorter than the van der Waals contact S···H (3·05 Å) (Pauling, 1960) by 0·17 Å; the same distance is obtained from the 1213 reflexions not corrected for secondary extinction. The direction of the S(2)–H(41–8) contact makes angles of 91° with the S(2)–C(0) and S(2)–Ni bonds, being normal to the plane of these two sulphur bonds. This short contact may correspond to a definite CH··S interaction or hydrogen bond.

It has been observed (Chatt, Duncanson & Venanzi, 1956*a*,*b*) that, in the dialkyldithiocarbamates, sulphur atoms, being conjugate to the strongly electron releasing NR_2 group, behave as electron acceptors in their *d*-orbitals. The induction effect of the propyl groups on the central part of the molecule might also be considered. Most of the C–H···X bonds [Pimentel & McClellan (1960) and further literature] concern more electronegative atoms X like oxygen and nitrogen; also a CH···Cl intramolecular interaction has been reported (Pinchas, 1955), but involving an aldehydic CH group. In the dipropyldithiocarbamate the mesomeric drift of electrons into the sulphur atom may favor the formation of a CH···S interaction or hydrogen bond.

The atom C(4) is involved in the CH---S interaction and this may contribute to the shortening of the C(4)–C(5) distance, owing to increased electron density in this bond. However, the value of this bond length, derived from the 1213 reflexions without the secondary extinction correction, is 1·51 Å, which is not significantly shorter than the normal single-bond length.

The S(2)–H(52–8′) distance (3·07 Å) has almost the theoretical value of the S···H van der Waals contact even if the S(2)–C(5–8′) distance (3·68 Å) is shorter than the van der Waals CH_2···S contact of 3·85 Å.

The Ni–C(4) distance (3·99 Å) of the nickel dipropyldithiocarbamate is much longer than the Ni–C(2) distance (3·54 Å) found in the nickel diethyldithiocarbamate.

The Ni–H(42–8) contact (3·24 Å) is the shortest Ni–H distance, but still very large indeed. This contact is nevertheless remarkable since it makes an angle of 93° with the Ni–S(1) bond and of 80° with the Ni–S(2) bond, being almost perpendicular to the Ni–S(1)–S(2) plane. Two H(42) atoms are centrosymmetrically situated in very elongated, almost octahedral sites with respect to the nickel atom, but at a much greater distance than in the nickel(II) bis(*N*,*N*-diethyldithiocarbamate), in which the shortest Ni–H distance which can be calculated from the given atom parameters (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965) is Ni–H(2a), 2·63 Å.

It seems therefore that in the crystal structures of both these nickel dithiocarbamates, as in copper(II) bis(*N*,*N*-diethyldithiocarbamate) (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965), the intermolecular CH hydrogen contacts with the central part of the molecule can play a definite role.

In nickel dipropyldithiocarbamate the more important hydrogen contacts concern two sulphur atoms centrosymmetric to the nickel atom, while in nickel diethyldithiocarbamate the hydrogen contact seems to concern the nickel atom.

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The Crystal Structure of Ethyl Carbamate

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The structure of ethyl carbamate (urethane, $C_2H_5.O.CONH_2$) has been determined using three-dimensional X-ray intensities measured with a proportional counter at two different temperatures. Atomic positions and anisotropic vibrational parameters have been refined by the method of least squares, and the vibrational parameters interpreted in terms of the rigid-body vibrations of the molecule.

Introduction

Several high-accuracy X-ray studies of the amide group have been made in recent years, including some in this laboratory using the three-circle diffractometer of Small & Travers (1961). In connection with these studies, the determination of the structure of ethyl carbamate is of interest in enabling a comparison to be made between the amidic C–O and C–N bond lengths in the carbamate group and those in other amides. Further interest lies in the length of the C–O bond connecting the carbamate group to the ethyl group, for studies of similar bonds in carboxylic acid esters (O'Gorman, Shand & Schomaker, 1950; Dougill & Jeffrey, 1953), tend to suggest that this bond is much longer than would be expected for a single C–O bond, although no really accurate evidence for this is yet available.

Intensity data measured for a crystal at room temperature *ca.* 25 °C showed that large atomic vibrations were present in ethyl carbamate crystals at this temperature. With a view to achieving greater accuracy from an increased number of measurements, the intensity measurements were repeated at −105 °C. Although more reflexions were observed at this temperature, the accuracy of the molecular parameters derived was not improved. Inaccuracies in the intensity measurements at the lower temperature arose from the design of the cooling system which was still under development at that time.

Crystal data

Crystals of ethyl carbamate, suitable for X-ray analysis, were obtained from a commercial sample by slow evaporation of an ethereal solution containing a small amount of light petroleum. The crystals were found to evaporate rapidly at normal temperatures, and it was necessary to seal them in Lindemann or 'Pantak' capillary tubes for all diffraction work. This process was usually hindered by the rather plastic nature of the crystals.

Preliminary Weissenberg photographs showed that ethyl carbamate crystallizes in the triclinic system, but accurate measurement of the unit-cell dimensions by the usual photographic methods was prohibited by a complete lack of observable reflexions at high Bragg angles. The suitability of diffractometer methods for precision cell dimension measurement has been demonstrated by Bond (1960) and so the instrument of Small & Travers was used in the following way for this purpose.

For a series of orders of reflexion from a certain set of crystal planes, line profiles were plotted with 2θ fixed and ω moving for each reflexion, the angles φ and χ being kept fixed throughout. To remove zero errors arising from both the instrument itself and missettings of φ and χ the 'observed' interplanar spacing for each measured value of θ_{obs} was plotted against

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