245. *The Crystal and Molecular Structure of Dichlorotetrakisthioureanickel,* $[(NH_2)_2CS]_4NiCl_2$.

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An *X*-ray crystal-structure analysis of the complex, $[(NH_2)_2CS]_4NiCl_2$, has been carried out at 110°K. There are two formula units in the tetragonal unit cell, $a = 9{\cdot}558$, $c = 8{\cdot}981$ Å, with space group $I4$. Each nickel atom is surrounded by four thiourea molecules related to each other by a 4-fold axis and two chlorine atoms which complete a distorted octahedron about the nickel. Three-dimensional anisotropic refinement gave the bond lengths (corrected for rotational oscillation) as Ni–Cl = 2·40 and 2·52 each ±0·02 Å, Ni–S = 2·462 ± 0·004 Å, S–C = 1·73 ± 0·03, and C–N = 1·33 ± 0·04 Å. The Cl–Ni–S angles are 96·7° and 83·3° both ±0·4°, Ni–S–C is 113·9° ± 0·8°, and the thiourea molecule is planar with N–C–N 121°, S–C–N 117° and 122° ±2°.

As part of a programme in which the dimensions of co-ordination complexes are measured and compared with those in the uncombined ligand molecules, the crystal structures of several compounds of sulphur have been determined.[1-4] The structure of dichlorotetrakisthioureanickel was chosen for this investigation because a preliminary examination by Nardelli, Cavalca, and Braibanti[5] had shown that the four molecules of thiourea were related crystallographically and that the nickel atom lay in a position (0,0,0) with no co-ordinate parameters, giving the most favourable conditions for an accurate determination of the parameters of the lighter atoms. Thiourea is a ligand molecule which has already been studied in this laboratory.[1]

Measurements were made on crystals at 110°K because a lower temperature enables more observations to be made and improves the ratio of the scattering powers of the light to those of the heavy atoms. Preliminary tests showed that there was no phase transformation when the temperature was lowered.

METHODS AND RESULTS

Crystal Data.—$C_4H_{16}N_8S_4Cl_2Ni$, $M = 434{\cdot}1$. Tetragonal, $a = 9{\cdot}558$, $c = 8{\cdot}981 \pm 0{\cdot}005$ Å at 110° ± 10°K, $U = 820{\cdot}5$ Å^3, $D_m = 1{\cdot}735$ (by flotation at room temperature), $Z = 2$, $D_c = 1{\cdot}756$, $F(000) = 444$. Space group $I4(C_4^5$, No. 79) determined by structure analysis. Cu-K_α radiation, single-crystal oscillation and Weissenberg photographs taken at 110° ± 10°K, absorption coefficient, $\mu = 92$ cm.$^{-1}$, absorption correction applied.

Three-dimensional Structure Determination.—The systematic absences and the relations between the intensities are consistent with three space groups, $I4/m$, $I\bar{4}$, and $I4$. Nardelli *et al.*[5] showed, by solving the $(hk0)$ projection, that the thiourea molecules were tilted with respect to the c-axis and could not lie in the mirror plane as required for $I4/m$. This projection also showed that the nickel and chlorine atoms all lay on the lines $(0,0,z)$ and $(\frac{1}{2},\frac{1}{2},z)$. Moderate agreement ($R = 0{\cdot}19$) was obtained for (hhl) reflections with a structure corresponding to the space group $I\bar{4}$; the molecule consisted of a nickel atom (at 0,0,0) surrounded by two chlorine atoms (at 0,0,2·4 and 0,0, −2·4 Å) and four sulphur atoms (at x_S, y_S,0 and the three positions related by the $\bar{4}$ symmetry), giving S–Ni = 2·45 Å. The S–C bond length was 1·64 Å and the C–N bond length 1·43 Å.

We started to refine this structure from the co-ordinates of Nardelli *et al.*[5] but with the average isotropic temperature factor, $U = 0{\cdot}008$ Å^2, which was about one-third of theirs to allow for the lower temperature.

For the first calculation of (hkl) structure factors, R was 0·29. After two cycles of isotropic refinement and two cycles of anisotropic refinement R fell to 0·16 and the largest shifts were

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[1] Kunchur and Truter, *J.*, 1958, 2551.

[2] Truter, *J.*, 1960, 997.

[3] Kunchur and Truter, *J.*, 1958, 3478.

[4] Truter and Rutherford, *J.*, 1962, 1748.

[5] Nardelli, Cavalca, Braibanti, *Gazzetta*, 1956, **86**, 942.

0·7 of the corresponding standard deviations. Refinement was discontinued, however, because the value of R was too high at this stage of refinement for a non-centrosymmetrical structure with the heavy atoms in special positions [cf. $R = 0{\cdot}08$ in tetrakisthioacetamide-copper(I)chloride,[4] also $I\bar{4}$]; moreover, $R_{(hk0)}$ was 0·09, *i.e.*, lower than $R_{(hkl)}$, whereas normally the R value for a centrosymmetrical projection in a non-centrosymmetric structure is higher than $R_{(hkl)}$. This, together with implausible bond lengths (S–C = 1·57, C–N = 1·39 and 1·45 Å) led us to conclude that the structure was wrong. Various explanations were considered, the correct one being that the space group is actually $I4$; this gives the same $(hk0)$ projection as $I\bar{4}$, but all the thiourea molecules are oriented in the same direction along the c-axis as shown in Figs. 1 and 2. Thus the chlorine atoms, each at $00z$, are independent and have different environments. With Nardelli *et al.*[5] co-ordinates refinement was started again in $I4$. For the first set of (hkl) structure factors R was 0·28; this was reduced in two cycles of isotropic refinement to 0·18 and by eight cycles of anisotropic refinement to 0·078.

At this stage the hydrogen atoms were included in positions which corresponded to a completely planar thiourea molecule as found by electron diffraction.[6] No improvement was recorded in R and the shifts indicated in the co-ordinates of the hydrogen atoms would have placed them in impossible positions. They were therefore omitted and refinement proceeded until the largest shift was 0·75 of the corresponding standard deviation. The results of this first refinement are shown in Tables 1 and 2.

TABLE 1.

Atomic co-ordinates (Å).

	First refinement			Second refinement				Minimum standard deviation		
	x	y	z	x	y	z	z'	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Ni	0·000	0·000	0·000	0·000	0·000	0·109	0	—	—	(0·004)
Cl(1) ...	0·000	0·000	2·409	0·000	0·000	2·505	2·397	—	—	0·005
Cl(2) ...	0·000	0·000	−2·490	0·000	0·000	−2·406	−2·514	—	—	0·005
S.........	0·272	2·428	−0·266	0·272	2·428	−0·178	−0·287	0·002	0·002	0·004
C	1·479	3·126	0·783	1·475	3·123	0·851	0·742	0·011	0·011	0·012
N(1) ...	1·883	4·370	0·475	1·881	4·364	0·557	0·449	0·011	0·010	0·013
N(2) ...	1·969	2·479	1·815	1·977	2·476	1·888	1·780	0·010	0·011	0·011

TABLE 2.

Thermal parameters (all units are 10^{-3} Å^2).

	U_{11}	σ	U_{22}	σ	U_{33}	σ	U_{12}	σ	U_{23}	σ	U_{13}	σ
					First refinement							
Ni....................	13		13		10							
Cl(1).................	15		15		6							
Cl(2).................	8		8		10							
S	12		9		9		−1		0		−3	
C	16		10		17		−0		−7		6	
N(1)	31		20		29		−14		8		−15	
N(2)	21		23		16		−12		−1		−15	
					Second refinement							
Ni....................	13	0·9	13	0·9	8	1·6	—		—		—	
Cl(1).................	16	1·4	16	1·4	10	2·1	—		—		—	
Cl(2).................	8	1·2	8	1·2	11	2·0	—		—		—	
S	13	0·8	9	0·8	8	1·0	−1	0·8	1	0·9	−3	1·0
C	14	5	12	5	18	5	0	4	−6	4	2	4
N(1)	30	6	19	5	33	6	−13	4	4	5	−14	5
N(2)	22	5	24	5	18	5	−13	4	−6	4	−14	4

The co-ordinates corresponded to a molecule with two different Ni–Cl bond lengths, 2·4 and 2·5 Å, and Cl–Ni–S angles significantly different from 90°. It was necessary to check that this was real and not an example of parameter interaction[7] causing refinement to an incorrect structure. This kind of structure, *i.e.*, one with a polar space group and atoms of differing

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[6] Dvoriankin and Vainstein, *Kristallografiya*, 1960, **5**, 589.

[7] Geller, *Acta Cryst.*, 1961, **14**, 1026.

scattering power, is most likely to show this effect and the z-co-ordinates are the most vulnerable, x and y having been fixed from a centrosymmetrical projection. One symptom of parameter interaction is that a different starting structure will refine to a different final one so that, in the worst cases, the structure is indeterminable. To test this a new starting structure was chosen; the x- and y-co-ordinates were again those of Nardelli *et al.*,[5] but the z-co-ordinates were chosen to make z_{Ni} and z_S both zero, and the dimensions of the thiourea molecule the same as those in the uncombined molecule,[1] *i.e.*, S–C 1·71 and C–N 1·33 Å, while z for Cl(1) was $+2{\cdot}4492$ and for Cl(2) $-2{\cdot}4492$ Å. The anisotropic thermal parameters were those resulting from the refinement of the previous set of co-ordinates. R was 0·17; four cycles of refinement reduced it to 0·08, and three further cycles were required to reduce it to 0·07 and give no more significant changes in the parameters. The main difference in the refinement procedures was that from the second set of co-ordinates the z-co-ordinate of nickel was allowed to vary.

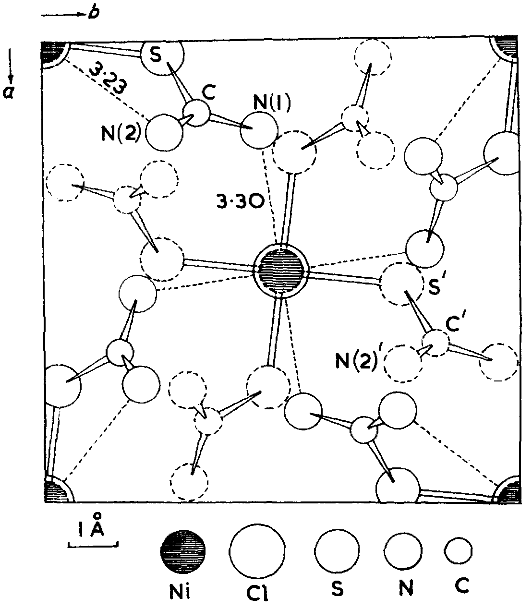

FIG. 1. The structure projected down the c-axis. Atoms shown by broken circles are in thiourea molecules co-ordinated to the nickel at $\frac{1}{2}$, $\frac{1}{2}$, $\sim\frac{1}{2}$. Broken lines show N–Cl contacts with their distances in Å.

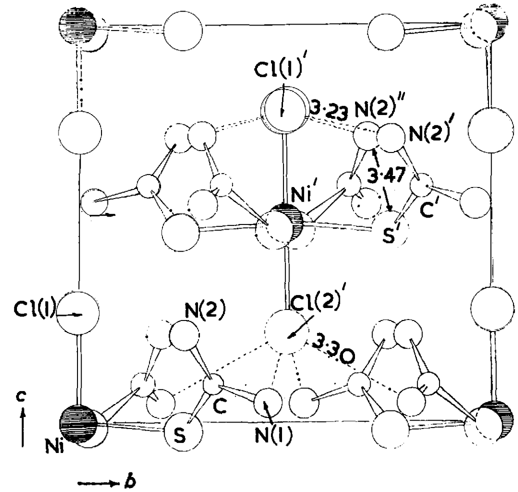

FIG. 2. The structure projected down the a-axis. Broken lines show N–Cl contacts with their distances in Å; the closest intermolecular N–S distance is indicated by an arrow.

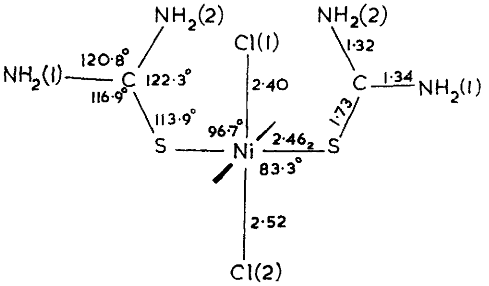

FIG. 3. Bond lengths, in Å, and angles in dichlorotetrakisthioureanickel. The uncertainty in these values is given in Table 5.

Results.—Table 1 shows the parameters after the first refinement, and the final parameters after the second refinement with their " minimum " standard deviations, a term explained below. To facilitate comparison of the two sets of results, the column z' is given corresponding to z with the origin for the second set of co-ordinates chosen to make $z'_{Ni} = 0$. While for the

TABLE 3.

Observed structure amplitudes and calculated structure factors ($F_c = A + iB$) × 10.

h	$\|F_o\|$	A	B
	*h*00		
2	325	372	0
4	1660	1779	0
6	549	547	0
8	668	659	0
12	337	356	0
	*h*10		
1	588	757	0
3	956	963	0
5	489	583	0
7	307	285	0
9	268	299	0
11	107	94	0
	*h*20		
2	146	158	0
4	626	708	0
6	128	108	0
8	666	653	0
10	300	281	0
12	427	518	0
	*h*30		
1	1357	1476	0
3	813	806	0
5	993	979	0
7	712	741	0
9	525	531	0
11	347	404	0
	*h*40		
2	720	876	0
4	1214	1336	0
6	467	490	0
8	627	600	0
10	166	145	0
	*h*50		
1	448	536	0
3	405	387	0
5	442	391	0
7	99	−68	0
9	386	434	0
	*h*60		
2	292	265	0
4	217	202	0
6	337	327	0
8	565	473	0
10	82	88	0
	*h*70		
1	941	949	0
3	492	462	0
5	1049	1019	0
7	292	314	0
9	607	684	0
	*h*80		
2	670	649	0
4	663	636	0
6	392	363	0
8	288	343	0
	*h*90		
1	492	506	0
5	316	290	0
	h,10,0		
2	302	290	0
4	232	200	0
6	241	232	0
	h,11,0		
1	609	617	0
3	210	207	0
5	606	716	0
	h,12,0		
2	450	506	0
	*h*01		
1	733	792	−36
3	497	458	−251
5	484	481	80
7	336	332	−39
9	121	130	35
11	79	83	1
	*h*11		
2	597	−592	−206
4	549	518	279
6	532	−543	−117
8	96	94	26
10	343	−331	6
12	139	144	6
	*h*21		
1	765	572	434
3	205	−155	104
5	177	166	−18
7	145	116	83
9	175	156	−26
11	137	121	−55
	*h*31		
2	274	110	223
4	864	826	−253
6	232	188	140
8	716	735	−105
10	127	100	40
	*h*41		
1	875	828	−244
3	98	82	−72
5	648	635	41
7	143	−15	−63
9	123	102	−56
	*h*51		
4	342	287	176
6	406	−414	−123
8	184	161	137
10	280	−305	−53
	*h*61		
1	388	288	138
3	331	−309	28
5	245	256	−33
9	317	262	−56
	*h*71		
2	79	19	−52
4	570	521	−88
6	285	248	68
8	375	303	−175
10	165	205	50
	*h*81		
1	723	763	−59
3	183	162	52
5	331	325	−88
9	159	161	−4
	h,10,1		
1	52	58	−13
3	304	−282	6
5	208	189	−34
	h,11,1		
2	322	289	−11
4	186	166	−51
	h,12,1		
1	336	362	−58
	*h*02		
0	1192	991	673
2	391	154	−283
4	464	321	−92
6	198	−63	191
8	194	135	−141
10	352	−349	32
	*h*12		
1	355	−266	−162
3	360	−103	349
5	415	−412	83
7	211	−167	125
9	361	−335	141
11	172	−166	15
	*h*22		
2	1462	−1317	276
4	174	−20	−123
6	567	−543	70
8	133	117	−73
10	202	−139	123
	*h*32		
1	248	201	111
3	103	−84	−102
5	298	278	−96
7	52	69	32
9	242	209	−164
	*h*42		
2	223	107	9
4	373	375	3
6	120	−79	103
8	139	151	−41
10	367	−325	96
	*h*52		
1	286	−31	−287
3	582	−500	262
5	84	−91	−31
7	462	−492	39
9	185	−96	144
11	262	−283	50
	*h*62		
2	609	−510	190
4	264	−182	−183
6	268	−241	179
10	129	−125	−83
	*h*72		
1	208	171	−91
3	90	42	87
5	302	341	−13
9	334	289	−33
	*h*82		
2	155	158	−26
4	111	96	−9
	*h*92		
1	137	147	3
3	531	−580	36
7	555	−466	141
	h,10,2		
2	214	−168	98
4	246	−192	70
6	98	−114	−1
	h,11,2		
1	150	106	−48
5	214	231	10
	*h*03		
1	989	925	−177
3	959	878	−163
5	603	572	−8
7	470	460	84
9	241	209	132
11	180	196	55
	*h*13		
2	368	184	270
4	442	426	15
6	353	−112	289
8	253	246	−109
10	296	−164	241
	*h*23		
1	727	327	588
3	340	160	273
5	435	387	167
7	242	162	161
9	258	280	14
11	238	241	19
	*h*33		
2	242	277	6
4	1145	1070	65
6	247	231	−85
8	768	798	96
10	163	158	8
	*h*43		
1	1199	1158	−96
3	453	398	−160
5	675	608	38
7	232	238	26
9	291	265	−61
11	171	31	211
	*h*53		
2	524	120	472
4	304	302	25
6	220	−54	224
8	115	116	90
10	155	−84	152
	*h*63		
1	322	303	81
3	274	−62	246
5	341	390	49
7	167	47	203
9	326	353	−7
	*h*73		
2	380	287	−221
4	629	617	104
6	259	254	−70
8	543	549	−83
	*h*83		
1	731	788	47
3	220	196	142
5	483	502	−194
7	260	80	199
	h,10,3		
1	166	180	−14
3	166	−84	121
5	234	243	67
	h,11,3		
2	316	304	26
4	248	276	16
	*h*04		
0	1499	1473	−19
2	681	689	342
4	1262	1236	−291
6	391	197	355
8	651	644	−167
10	184	115	131
	*h*14		
1	739	802	46
3	650	418	488
5	388	354	167
7	373	157	340
9	201	159	158
11	184	93	146
	*h*24		
2	206	189	151
4	552	497	128
6	258	180	185
8	517	533	−80
10	253	95	213
	*h*34		
1	807	828	34
3	788	686	136
5	745	725	−138
7	496	496	7
9	676	556	−114
11	388	352	−87
	*h*44		
2	603	495	310
4	908	886	−143
6	426	315	258
8	479	473	−27
10	214	101	142
	*h*54		
1	647	617	−106
3	376	119	289
5	376	360	110
7	179	66	179
9	262	180	165

TABLE 3. (*Continued.*)

h	$\lvert F_o \rvert$	*A*	*B*
	*h*64		
2	282	123	243
4	456	431	−25
6	243	68	225
8	478	425	−72
	*h*74		
1	811	802	−193
3	465	255	276
5	695	713	−133
7	333	319	19
	*h*84		
2	504	491	39
4	468	464	−59
6	392	351	53
8	279	261	64
	*h*94		
1	299	306	92
3	114	93	59
5	308	254	107
7	175	−100	159
	h,10,4		
2	253	160	162
4	208	121	144
	h,11,4		
1	577	534	−137
3	180	162	97
	*h*05		
1	403	315	−187
3	375	300	−270
5	246	213	41
9	97	−55	95
11	73	6	70
	*h*15		
2	450	−294	317
4	152	122	5
6	543	−481	227
8	170	174	14
10	535	−414	178
	*h*25		
1	508	−282	389
3	412	−268	279
5	178	−46	159
7	170	−136	99
	*h*35		
2	169	37	161
4	358	284	−231
6	115	140	47
8	247	185	−174
10	43	43	23
	*h*45		
1	492	417	−236
3	217	179	−108
5	205	155	−136
9	145	106	−83
	*h*55		
2	520	−452	228
4	200	118	163
6	375	−388	149
8	94	−28	93
	*h*65		
1	143	48	110
3	448	−346	272
7	309	−190	192
9	152	64	−119
	*h*75		
2	226	204	−81
4	168	99	−136
8	322	227	−165
	*h*85		
1	242	218	−175
3	109	−80	48
5	358	304	−190
7	226	−201	104
	*h*95		
2	147	−125	33
4	229	−109	184
6	258	−233	101
	h,10,5		
1	62	49	−27
3	331	−228	200
	*h*06		
0	250	240	−108
2	105	85	−51
4	479	436	−99
6	195	−210	59
8	291	256	−123
10	239	−131	208
	*h*16		
1	106	106	61
3	337	−211	254
5	276	−135	228
7	249	−170	208
9	367	−225	248
	*h*26		
2	681	−351	512
4	142	73	−153
6	423	−190	368
8	183	128	−137
10	220	−186	106
	*h*36		
1	151	105	−116
3	139	104	118
5	330	243	−233
7	76	42	−63
9	306	235	−158
	*h*46		
4	331	286	−141
6	189	−137	164
8	226	144	−107
	*h*56		
1	250	231	−149
3	438	−292	329
	*h*66		
2	472	−267	350
4	85	90	11
	*h*76		
1	238	247	−67
3	108	−105	38
	*h*86		
2	91	64	−67
4	193	130	−99
	*h*96		
1	166	22	−170
3	398	−176	323
	h,10,6		
2	220	−156	156
	*h*07		
1	646	638	−63
3	723	706	−56
5	367	383	98
7	392	418	12
9	275	188	171
	*h*17		
2	677	276	564
4	388	346	3
6	401	187	425
8	355	262	197
	*h*27		
1	325	135	287
3	442	197	371
5	409	277	285
7	328	185	147
9	271	261	32
	*h*37		
2	406	258	243
4	765	694	−142
6	325	235	147
8	609	513	−204
	*h*47		
1	742	707	−122
3	510	481	107
5	465	448	−152
7	417	304	204
	*h*57		
2	322	170	276
4	309	202	209
	*h*67		
1	295	235	190
3	495	116	391
	*h*77		
2	480	361	126
4	571	472	−98
	*h*87		
1	587	487	−233
3	243	201	120
	*h*97		
2	189	210	161
	*h*08		
0	617	398	−530
2	429	285	302
4	469	395	−239
6	200	165	138
8	331	313	−74
	*h*18		
1	341	280	185
3	254	92	246
5	238	127	229
7	336	43	317
	*h*28		
2	416	1	411
4	335	343	88
5	416	−29	385
8	304	291	−94
	*h*38		
1	340	345	−127
3	247	202	202
5	471	361	−165
7	295	270	−91
	*h*48		
2	279	234	144
4	495	351	−223
6	249	98	183
	*h*58		
1	328	338	93
3	313	42	276
	*h*68		
2	334	−30	309
4	325	252	183
	*h*78		
1	326	309	−145
3	204	129	145
	*h*88		
2	220	211	−25
	*h*09		
1	149	50	−172
3	134	35	−125
5	89	−47	−72
7	57	−15	−60
	*h*19		
2	471	−322	401
4	166	72	−123
6	511	−247	409
	*h*29		
1	156	−169	79
3	317	−178	248
5	268	−226	115
7	95	−87	30
	*h*39		
2	142	−71	104
4	259	−36	−247
	*h*49		
1	251	−22	−237
5	252	72	−225
	*h*59		
2	292	−217	185
4	71	−75	7
	*h*69		
1	88	−95	3
3	407	−207	324
	*h*79		
2	51	−47	22
	h,0,10		
0	478	329	−339
4	278	186	−214
	h,1,10		
1	127	67	121
3	145	40	162
5	222	23	235
	h,2,10		
2	516	59	515
	h,3,10		
1	193	186	−66
3	65	−19	48
5	181	168	−150
	h,4,10		
4	283	210	−188
	h,5,10		
1	72	73	0
3	289	53	328
	h,0,11		
1	292	296	−2
3	294	314	0
	h,1,11		
2	373	159	360
	h,2,11		
1	334	243	264
3	287	207	348
	h,3,11		
2	243	188	279

x- and y-co-ordinates the two sets of refinements give the same results within the " minimum " standard deviation, for the z-co-ordinates the differences may be as much as four times the corresponding " minimum " standard deviation.

This difference in z values and the slow convergence of the refinement indicate that there is some parameter interaction. In the least-squares refinement procedure we used [8] the diagonal approximation; allowance has been made for interaction between the overall temperature factor and the scale and, for any given atom, for interaction between its co-ordinate parameters and for interaction between its thermal parameters. In the full least-squares matrix the interaction between the co-ordinate and the thermal parameters of one atom are allowed for, and so too are the interactions between the parameters of one atom and those of another. One result of using the diagonal approximation instead of the full matrix is that the calculated standard deviations are less than they should be, so we have referred to them as the " minimum " standard deviations. Internal evidence suggests that a conservative estimate of the error would be given by doubling the " minimum " value for $\sigma(x)$ and $\sigma(y)$ and multiplying $\sigma(z)$ by four; this has been taken as the uncertainty.

Table 2 shows the thermal parameters after the first and the second refinement (the first were used as the starting parameters for the second refinement). These are the same to within twice the " minimum " standard deviation, also shown in Table 2, indicating that they are not very sensitive to changes in the co-ordinates. U_{11}, U_{22}, and U_{33} are the mean square amplitudes of vibration parallel to the a^*-, b^*-, and c^*-axes, respectively, and, with U_{12}, U_{23}, and U_{13}, define the magnitude and orientation of the ellipsoid of vibration with respect to the crystallographic axes.

Table 3 shows the final observed structure amplitudes and the real and imaginary parts of the calculated structure factors for the parameters given in Tables 1 and 2 as the results of the second refinement.

An analysis [8] of the molecular vibration parameters was carried out. The whole molecule was assumed to move as a rigid body, and internal consistency indicated that the assumption was justified. The calculation gave root-mean-square amplitudes of translatory motion of the molecule as 0·07 Å parallel to c and 0·09 Å in the ab-plane, and the r.m.s. amplitudes of rotational oscillation as 1·9° ± 0·2° about c and 1·8° ± 0·2° about [110]. The corrected co-ordinates were corrected for rotational oscillation, the largest correction being 0·004 Å. The corrected co-ordinates are given in Table 4, these, but to 4 decimal places as given by the computer, were used to calculate the bond lengths and angles, the van der Waals separations, and the plane through the atoms S, C, N(1) and N(2).

TABLE 4.

Corrected atomic co-ordinates (Å).

	x	y	z		x	y	z
Ni	0·000	0·000	0·108	C	1·477	3·126	0·851
Cl(1)	0·000	0·000	2·507	N(1)	1·882	4·368	0·557
Cl(2)	0·000	0·000	−2·408	N(2)	1·979	2·478	1·890
S	0·272	2·430	−0·179				

The bond lengths and angles are given in Fig. 3. Values for the uncertainty, calculated from $2\sigma(x)$, $2\sigma(y)$, and $4\sigma(z)$ of Table 1, are shown in Table 5. The thiourea molecule is planar; the equation of the plane is

$$0{\cdot}719x - 0{\cdot}375y - 0{\cdot}585z + 0{\cdot}548 = 0$$

and the largest deviation is 0·002 Å for the carbon atom. The nickel atom lies 0·55 Å from this plane so that the Ni–S bond makes an angle of 77° with the normal to the plane.

Each nitrogen atom has one chlorine atom as a neighbour at a distance short enough to represent a hydrogen bond, 3·23 and 3·30 Å as shown in Figs. 1 and 2. For N(2) the chlorine is Cl(1) of the same molecule, the angle C–N(2)–Cl(1) is 107·0°. For N(1) the chlorine is Cl(2)

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[8] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, " Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, Oxford, 1961, p. 32.

of the molecule related to the original one by body-centring, *i.e.*, Cl(2)′, and the angle C–N(1)–Cl(2)′ is 106·3°. Neither chlorine atom lies in the plane of the thiourea molecule, the distances being 0·86 and 1·0 Å for Cl(1) and Cl(2)′, respectively.

TABLE 5.

Uncertainty in bond length (Å) and angles.

Ni–Cl	0·02	S–C	0·03	Cl–Ni–S	0·4°	S–C–N	1·5°
Ni–S	0·004	C–N	0·04	Ni–S–C	0·8	N–C–N	2·2

There is only one other contact of less than 3·5 Å between two atoms which are not bonded to the same atom, that is a distance 3·47 Å from N(2) to the sulphur atom of another thiourea molecule, as shown in Fig. 2. Although this length is within the range found for the hydrogen bonds N–H • • • S in thioacetamide,[2] it is unlikely that a hydrogen atom is situated along this direction because the angles at N(2) are C′–N(2)′–S″ 65·5° and Cl(1)′–N(2)′–S″ 88·3°.

Each chlorine atom is bonded to one nickel atom and hydrogen-bonded by four nitrogen atoms. For Cl(1) the angle Ni–Cl(1)–N(2) is 79° while for Cl(2) the Ni–Cl(2)–N(1)′ angle is 117·5°.

DISCUSSION

The structure as a whole consists of molecules, all oriented in the same way and probably held by Cl • • • N hydrogen bonds as well as by van der Waals forces. Our cell dimensions are smaller than those found at room temperature;[5] the ratio, 1 : 1·0065, is the same for the *a*-axis as for the *c*-axis, an observation consistent with the nearly isotropic thermal motion we found for the heavy atoms (Table 2) and the lack of any extensive system of strong bonding in the structure.

For comparisons of bond lengths to be meaningful it is essential that only the results of three-dimensional determinations be considered. (A striking example of the discrepancy between the results of two- and three-dimensional work has recently been published by Grant and Speakman.[10]) Since 1957 when we made a preliminary report[11] on the investigation of the dimensions of thioamides free and as complexes, a number of these complexes have been subjected to three-dimensional crystal-structure analysis; the results are summarised in Table 6. The standard deviations quoted in Table 6 are those given by the authors of the papers; the value ±0·01 Å for tristhioureacopper(I) chloride seems

TABLE 6.

Bond lengths (Å) in thioamide ligands.

Compound *	C–S	C–N	$\bar{1}$ †	*R*	Ref.	Remarks
Thiourea	1·70 ± 0·02	1·33 ± 0·02	Yes	0·11	1	‡
$(Thio)_4Cl_2Ni$	1·73 ± 0·03	1·32, 1·34 ± 0·04	No	0·07	—	
$(Thio)_2(NCS)_2Ni$	1·77	1·31, 1·31	Yes	0·16	*a*	§
$[(Thio)_3Cu]Cl$	1·80—1·83 ± 0·01	1·24—1·46 ± 0·01	No	0·19	*b*	¶
$(Thio)_2Cl_2Zn$	1·78 ± 0·02	1·26, 1·30 ± 0·03	Yes	0·15	3	
Thioacetamide	1·713 ± 0·006	1·324 ± 0·008	Yes	0·12	2	
$[(Thacet)_4Cu]Cl$	1·71 ± 0·02	1·31 ± 0·02	No	0·09	4	

* Thio = thiourea; Thacet = thioacetamide. † An indication of the presence of a centre of symmetry in the crystal structure. ‡ These results differ slightly from the published values[1] because they have been obtained by (*a*) carrying out a refinement of the structure of thiourea by the same methods and with the same scattering factors as in the present work, (*b*) including the hydrogen atoms, and (*c*) using the results to calculate the correction for rotational oscillation by Cruickshank's revised procedure.[9] § Partial three-dimensional data. ¶ Three crystallographically independent thiourea molecules.

(*a*) Nardelli, Braibanti, and Fava, *Gazzetta*, 1957, 1209. (*b*) Knobler, Okaya, and Pepinsky, *Z. Krist.*, 1959, **111**, 385.

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[9] Cruickshank, *Acta Cryst.*, 1961, **14**, 896.
[10] Grant and Speakman, *Acta Cryst.*, 1962, **15**, 292.
[11] Truter, *Acta Cryst.*, 1957, **10**, 785.

to us to be optimistic; not only was refinement not continued beyond $R = 0{\cdot}186$, but the structure is non-centrosymmetrical and so likely to exhibit parameter interaction. Table 6 shows that in two complexes the dimensions of the ligand molecules have not changed significantly, whereas for the others there appears to be an increase in the C–S bond length. There is not yet sufficient really accurate work for it to be possible to decide whether the dimensions of the ligand do vary from complex to complex. If they do vary for the thioamides their behaviour is in marked contrast to that of biuret. All bond lengths of the biuret portion of the molecule are the same in biuret hydrate,[12] in the zinc complex [13] (in which oxygen is the ligand atom), and in a copper complex [14] (in which nitrogen is the ligand atom).

In dichlorotetrakisthioureanickel, as in all the other complexes of Table 6 in which the sulphur atom is bound to one metal atom, the metal lies significantly out of the plane of the thioamide. There is some evidence for N–Cl hydrogen bonding in all the suitable complexes, although in dichlorobisthioureazinc the bonding is confined to one intramolecular N–Cl hydrogen bond and the shortest intermolecular approaches are between chlorine and sulphur. This type of bonding is presumably not strong enough to be structure-determining.

The most interesting feature of the results is the non-centrosymmetrical environment about the nickel atom. A model reveals no reason for the preference for 4 instead of $\bar{4}$ symmetry; indeed, the latter would give a flattened tetrahedron instead of a pyramidal arrangement of hydrogen bonds about the chlorine atoms and seems more likely. There is no doubt that the effect is real. The centre of the square containing the four sulphur atoms is 0·23 Å from the mid-point of the line joining the two chlorine atoms, so that there is no position in which the nickel atom could have a centrosymmetrical arrangement of bonds. The distance between the mid-points is changed by only 0·01 Å when the z-co-ordinate of nickel is treated as a parameter in the refinement (see Table 1). The observed position of the nickel atom is not on either of the mid-points, or on the line joining the two mid-points. It is, in fact, closer to Cl(1), making Ni–Cl(1) shorter than Ni–Cl(2) by 0·12 Å, which is significant ($\Delta/\sigma = 4{\cdot}2$). A complex with stereochemistry similar to this has been found [15] in $Ni(NH_3)_3(NCS)_2$ in which there are five bonds to nitrogen, forming a square pyramid (Ni–N $= 2{\cdot}06 \pm 0{\cdot}04$) and the sixth to sulphur, 2·50 Å, which is long enough to represent a purely ionic separation. There does not appear to be any preferred symmetry for the environment about nickel(II) in spin-free complexes; for example, there may be none if it is not required by the space group, as in dihydrogen aquoethylenediaminetetra-acetatonickel,[16] a 4-fold axis as in the present compound, or a centre of symmetry as in di-isothiocyanatobisthioureanickel.[16a]

Although only a few of the structures in which nickel is known to be co-ordinated to sulphur have been investigated by three-dimensional methods, it is already clear that the nickel atom possesses at least two different radii. In 4-co-ordinated, diamagnetic complexes, the Ni–S distance lies within the range 2·1—2·3 Å, *e.g.*, 2·16 Å in bisthiosemicarbazidatonickel,[17] while in 6-co-ordinated complexes the Ni–S distance lies within the range 2·4—2·6 Å, *e.g.*, 2·46 Å in the present work. 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.

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[12] Hughes, Yakel, and Freeman, *Acta Cryst.*, 1961, **14**, 345.

[13] Nardelli, Fava, and Giraldi, Proc. 7th Internat. Conference on Co-ordination Chemistry, Stockholm, 1962, p. 211.

[14] Freeman, Smith, and Taylor, *Acta Cryst.*, 1961, **14**, 407.

[15] Poraj-Koshitz, *Proc. Inst. Crystallogr.*, 1954, **10**, 117.

[16] Smith and Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 549.

[16a] Nardelli, Braibanti, and Fava, *Gazzetta*, 1957, 1209.

[17] Calvalca, Nardelli, and Fava, Proc. 7th Internat. Conference on Co-ordination Chemistry, Stockholm, 1962, p. 211.

EXPERIMENTAL

The method of Rosenheim and Meyer[18] was used to prepare the compound. It crystallised as olive-green needles elongated parallel to *c*.

All *X*-ray photographs were taken with Cu-K_α radiation. The crystal was cooled in a stream of nitrogen with an apparatus adapted from that described by Robertson.[19] No phase transformation took place on cooling. From time to time the temperature at the site of the crystal was measured and found to lie within the range 100—120°K.

Accurate values of the unit-cell dimensions were obtained from Weissenberg photographs on which the diffraction pattern of a copper wire was superimposed for calibration. Equi-inclination Weissenberg photographs were taken about the *a*- and the *c*-axis up to the fourth and the fifth layer line, respectively; 404 of a possible 470 independent reflections gave measurable intensities. A multiple-film technique was used and the intensities of the spots were estimated visually with the aid of a calibration strip. For non-zero layers the Phillips spot-shape correction factor[20] was applied; this, and the application of Lorentz and polarisation corrections, were carried out on the Leeds University Ferranti Pegasus computer with a programme written by Mr. J. G. F. Smith. No absorption correction was applied to the intensities measured about the *c*-axis because the crystal was 0·1 mm. in diameter; but the crystal set about the *a*-axis had been cut to form a cube of side 0·2 mm., so these intensities were corrected for absorption as for a sphere.[21] Correlation of the layer lines gave a set of relative values for $F(hkl)$, the first scale factor was obtained by comparison of $F(hk0)$ with the values calculated by Nardelli *et al.*[5] and the scale factor was one of the parameters in the refinement.

The scattering factors were those of Berghuis *et al.*[22] for carbon, nitrogen, and chloride ion and that of Watson and Freeman[23] for Ni^{2+} with a correction for the real part of the anomalous dispersion;[24] for sulphur the corrected scattering factor of Tomiie and Stam[25] was used. Refinement was carried out by the method of least squares on the Pegasus computer with programmes written by Cruickshank *et al.*[8] The function minimised was $R' = w(|F_o|) - |F_c|)^2$, where w was taken as $1/|F_o|$. Analysis of the molecular vibration and correction for rotational oscillation were carried out on the computer with programmes written by Mr. Bujosa and Dr. Cruickshank.[8]

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[18] Rosenheim and Meyer, *Z. anorg. Chem.*, 1906, **49**, 13.
[19] Robertson, *J. Sci. Instr.*, 1960, **37**, 41.
[20] Phillips, *Acta Cryst.*, 1954, **7**, 746.
[21] International Tables for X-ray Crystallography, Vol. II, 1959, Kynoch Press, Birmingham.
[22] Berghuis, Haanappel, Potters, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[23] Watson and Freeman, *Acta Cryst.*, 1961, **14**, 27.
[24] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.
[25] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.