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The Crystal and Molecular Structure of Bis(thioacetamide)nickel(II) Thiocyanate

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The crystal structure of bis(thioacetamide)nickel(II) thiocyanate, $Ni[SC(CH_3)NH_2]_2(NCS)_2$, has been studied by three-dimensional Fourier methods. The habit of the crystals is rhombohedral, yet the Bravais lattice is *P*. There are three formula units in the unit cell: $a = 9·463 \pm 0·009$, $c = 12·627 \pm 0·022$ Å, space group $P3_121$. Coordination around each Ni atom is octahedral and involves two sulphur atoms from two thioacetamide molecules (Ni–S, 2·45 ± 1 Å), two sulphur (Ni–S, 2·55 ± 1 Å) and two nitrogen atoms (Ni–N, 2·02 ± 1 Å) from four NCS groups which are in a bridging position. The nitrogen atoms are *trans* with respect to the plane of the sulphur atoms and the thioacetamide molecules lie on adjacent corners of the coordination polyhedron. The octahedra are linked in helical chains running along a 3_1 axis. The thioacetamide molecules are planar and tilted with respect to the coordination plane of the sulphur atoms. The structure is compared with those of the similar compounds bis(thiourea)Ni(II) and bis(ethylenethiourea)Ni(II) thiocyanates.

Introduction

In our programme of work on the determination of the crystal structures of metal-complex compounds of ligands containing sulphur as donor atom, results for Ni*tu*$_2$(NCS)$_2$ [*tu* = thiourea, $SC(NH_2)_2$] (Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966) and Ni*etu*$_2$(NCS)$_2$ [*etu* = ethylenethiourea = $SC(NHCH_2)_2$] (Nardelli, Fava Gasparri, Musatti & Manfredotti, 1966) have already been published. In the present paper

Table 1. *Final atomic fractional coordinates* (× 10⁴), *thermal parameters* (× 10 Å²) *with e.s.d.'s and ratios* (*e.s.d.*)/(*coordinate shift*)

	x/a	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	*r(x)*	*r(y)*	*r(z)*
Ni	2211 ± 6	0	3333	39 ± 9	45 ± 9	34 ± 1	−3 ± 4	−1 ± 4	24 ± 10	∞	—	—
S(1)	5000 ± 9	2308 ± 9	3257 ± 3	23 ± 6	38 ± 6	35 ± 0	−7 ± 3	1 ± 3	16 ± 7	∞	1	3
S(2)	2037 ± 10	1241 ± 12	6976 ± 2	35 ± 7	37 ± 7	23 ± 1	−5 ± 2	−3 ± 2	22 ± 8	10	∞	2
N(1)	2335 ± 38	339 ± 33	4916 ± 6	38 ± 26	37 ± 25	27 ± 2	−5 ± 10	−3 ± 10	21 ± 30	6	16	∞
N(2)	5778 ± 48	805 ± 53	1851 ± 13	44 ± 32	47 ± 30	50 ± 3	−16 ± 12	−3 ± 12	20 ± 37	∞	13	13
C(1)	6243 ± 43	1970 ± 56	2453 ± 12	43 ± 34	38 ± 32	34 ± 3	−3 ± 13	−3 ± 13	25 ± 39	22	8	∞
C(2)	2226 ± 34	757 ± 45	5763 ± 16	25 ± 22	27 ± 22	29 ± 1	−5 ± 10	−2 ± 10	13 ± 26	17	22	8
C(3)	7989 ± 40	3276 ± 47	2395 ± 16	35 ± 28	36 ± 29	50 ± 1	0 ± 15	−6 ± 15	12 ± 35	4	47	16

Table 2. *Atomic peak heights* (e.Å⁻³), *and curvatures* (e.Å⁻⁵)

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Ni	obs.	53·1	451	398	518	−11	4	207
	calc.	52·1	447	398	518	−10	4	203
S(1)	obs.	30·4	252	246	281	−34	19	116
	calc.	29·3	250	247	283	−31	17	116
S(2)	obs.	33·4	291	280	338	−6	−10	157
	calc.	32·5	291	280	336	−4	−9	155
N(1)	obs.	9·7	54	66	118	−10	4	25
	calc.	9·3	54	66	117	−10	4	25
N(2)	obs.	8·8	66	59	66	−7	6	35
	calc.	8·6	67	59	68	−6	6	35
C(1)	obs.	8·3	64	51	69	0	−4	29
	calc.	8·0	63	50	68	1	−4	29
C(2)	obs.	9·9	90	84	64	6	−7	45
	calc.	9·4	90	84	63	6	−7	45
C(3)	obs.	8·1	60	52	54	−1	1	25
	calc.	7·9	61	54	55	−2	2	26
	e.s.d.	0·5	5	5	5	3	3	4

the structure of the similar compound Ni*tam*$_2$(NCS)$_2$ [*tam* = thioacetamide = SC(CH$_3$)NH$_2$] is described. The comparison of these three structures is interesting in terms of the influence of the nature of the ligands on the behaviour of the thiocyanate group in these compounds in which the oxidation state of the metal atom, the coordination around it and the number of thiocyanate groups are the same. On the other hand, it was evident, even from the preliminary crystal data alone, that these structures were quite different and it was not possible to guess the structural role of the ligands in them.

The thioacetamide complex is interesting also from a crystallographic point of view as the translation lattice is *P* while its habit is rhombohedral, so it is an exception to the Bravais–Donnay rule, as observed by Professor J. D. H. Donnay (private communication).

Table 3. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'

h	k	l	$10F_o$	$10F_c$	α°
0	0	3	1048	1376	0
0	0	6	876	1091	0
0	0	9	469	488	0
0	0	12	344	356	0
0	0	15	41-	46	180
1	0	0	500	571	0
1	0	1	821	1087	240
1	0	2	456	407	300
1	0	3	57-	28	180
1	0	4	402	391	240
1	0	5	702	729	300
1	0	6	298	289	0
1	0	7	532	533	240
1	0	8	451	445	300
1	0	9	75-	11	180
1	0	10	116	109	240
1	0	11	255	235	300
1	0	12	138	138	180
1	0	13	240	232	240
1	0	14	52-	46	300
1	0	15	164	169	180
1	0	16	83	100	240
2	0	0	667	497	180
2	0	1	129	43	59
2	0	2	737	686	300
2	0	3	481	321	180
2	0	4	65-	55	239
2	0	5	159	86	300
2	0	6	71-	33	180
2	0	7	72-	20	240
2	0	8	117	92	300
2	0	9	75-	25	180
2	0	10	171	166	60
2	0	11	71-	0	180
2	0	12	66-	56	180
2	0	13	115	100	240
2	0	14	77	63	120
2	0	15	37-	1	0
2	0	16	17-	48	240
3	0	0	864	790	180
3	0	1	157	131	60
3	0	2	568	529	120
3	0	3	306	220	180
3	0	4	210	153	60
3	0	5	533	487	120
3	0	6	287	256	0
3	0	7	86	67	60
3	0	8	308	266	120
3	0	9	340	304	0
3	0	10	73-	61	239
3	0	11	129	110	120
3	0	12	165	154	0
3	0	13	101	85	239
3	0	14	135	124	120
3	0	15	77	90	0
4	0	0	807	784	0
4	0	1	186	88	240
4	0	2	204	167	120
4	0	3	798	756	0
4	0	4	93	49	60
4	0	5	354	300	120
4	0	6	820	834	0
4	0	7	75-	5	233
4	0	8	108	85	120
4	0	9	515	508	0
4	0	10	70-	60	240
4	0	11	65-	17	119
4	0	12	368	376	0
4	0	13	48-	0	0
4	0	14	73-	80	300
5	0	0	300	217	0
5	0	1	608	578	240
5	0	2	538	508	120
5	0	3	73-	23	0
5	0	4	380	352	240
5	0	5	131	101	121
5	0	6	75-	36	0
5	0	7	226	195	239
5	0	8	73-	28	300
5	0	9	70-	26	180
5	0	10	169	182	240
5	0	11	220	202	300
5	0	12	92	88	0
5	0	13	92	94	240
5	0	14	74	95	300
6	0	0	198	163	180
6	0	1	75	68	240
6	0	2	271	243	120
6	0	3	243	176	180
6	0	4	102	99	59
6	0	5	88	59	121
6	0	6	242	223	180
6	0	7	71-	43	59
6	0	8	67-	21	298
6	0	9	120	97	180
6	0	10	96	91	59
6	0	11	48-	5	292
6	0	12	63	49	180
6	0	13	35	49	60
7	0	0	371	373	180
7	0	1	144	134	60
7	0	2	183	172	120
7	0	3	300	271	180
7	0	4	96	90	60
7	0	5	209	196	120
7	0	6	247	221	180
7	0	7	63-	19	59
7	0	8	213	210	120
7	0	9	52-	67	180
7	0	10	44-	30	60
7	0	11	92	87	121
7	0	12	53	69	180
8	0	0	146	134	0
8	0	1	66-	44	60
8	0	2	66-	37	121
8	0	3	171	177	0
8	0	4	91	58	60
8	0	5	173	150	120
8	0	6	144	144	0
8	0	7	50-	5	239
8	0	8	127	131	121
8	0	9	108	104	0
8	0	10	28-	0	0
9	0	0	95	98	0
9	0	1	203	222	240
9	0	2	83	96	120
9	0	3	85	72	0
9	0	4	151	158	240
9	0	5	43-	19	121
9	0	6	44	7	0
9	0	7	80	102	240
9	0	8	74	108	120
10	0	0	100	121	0
10	0	1	91	87	239
10	0	2	44	27	301
10	0	3	62	90	0
10	0	4	51	44	240
10	0	5	53	71	301
0	1	1	288	252	300
0	1	2	838	934	240
0	1	3	824	851	0
0	1	4	385	273	300
0	1	5	854	992	240
0	1	6	288	232	0
0	1	7	245	208	120
0	1	8	639	676	240
0	1	9	91	54	180
0	1	10	208	188	120
0	1	11	368	376	240
0	1	12	72-	17	0
0	1	13	101	95	121
0	1	14	215	219	239
0	1	15	42-	21	180
0	1	16	25-	30	120
1	1	0	766	612	56
1	1	1	634	485	294
1	1	2	328	246	91
1	1	3	424	319	46
1	1	4	493	384	139
1	1	5	238	200	248
1	1	6	320	283	109
1	1	7	339	301	138
1	1	8	276	254	246
1	1	9	173	171	69
1	1	10	270	269	141
1	1	11	160	152	241
1	1	12	177	165	83
1	1	13	171	174	187
1	1	14	100	94	162
1	1	15	69	62	106
1	1	16	72	119	184
2	1	0	790	796	135
2	1	1	463	425	298
2	1	2	594	455	4
2	1	3	151	42	335
2	1	4	472	376	293
2	1	5	452	364	350
2	1	6	324	276	95
2	1	7	313	294	261
2	1	8	129	100	326
2	1	9	257	229	33
2	1	10	212	195	266
2	1	11	82	75	40
2	1	12	165	152	84
2	1	13	175	133	228
2	1	14	85	71	176
2	1	15	93	96	44
3	1	0	209	123	202
3	1	1	1029	1034	343
3	1	2	420	333	122
3	1	3	333	261	198
3	1	4	683	626	351
3	1	5	404	345	117
3	1	6	66	59	51
3	1	7	608	591	343
3	1	8	346	307	125
3	1	9	148	128	355
3	1	10	197	197	340
3	1	11	158	147	135
3	1	12	79	57	32
3	1	13	137	140	350
3	1	14	94	103	190
3	1	15	27-	14	133
4	1	0	157	141	13
4	1	1	450	386	318
4	1	2	459	421	194
4	1	3	113	106	41
4	1	4	342	305	348
4	1	5	323	305	232
4	1	6	340	322	340
4	1	7	289	283	342
4	1	8	187	174	242
4	1	9	187	180	2
4	1	10	160	159	340
4	1	11	146	157	259
4	1	12	149	149	328
4	1	13	102	104	17
4	1	14	118	152	259
5	1	0	243	243	51
5	1	1	165	134	217
5	1	2	259	210	174
5	1	3	149	117	37
5	1	4	83	48	126
5	1	5	82	36	295
5	1	6	102	92	51
5	1	7	147	136	335
5	1	8	74-	2	135
5	1	9	82	65	180
5	1	10	79	68	17
5	1	11	137	128	298
5	1	12	36	35	63
5	1	13	34-	28	291
6	1	0	229	226	129
6	1	1	238	237	224
6	1	2	59	29	25
6	1	3	178	154	130
6	1	4	146	154	232
6	1	5	143	89	46
6	1	6	232	207	150
6	1	7	126	137	244
6	1	8	105	97	336
6	1	9	110	111	178
6	1	10	103	111	279
6	1	11	77	82	316
6	1	12	56	70	228
7	1	0	169	177	131
7	1	1	170	182	48
7	1	2	155	184	138
7	1	3	213	234	145
7	1	4	151	160	65
7	1	5	216	238	100
7	1	6	202	213	145
7	1	7	84	76	15
7	1	8	157	192	131
7	1	9	55	68	197
7	1	10	93	112	17
7	1	11	118	193	120
8	1	0	90	101	50
8	1	1	63-	58	58
8	1	2	84	97	257
8	1	3	132	154	85
8	1	4	56	63	79
8	1	5	59	64	217
8	1	6	105	126	41
8	1	7	42	44	32
8	1	8	59	64	170
8	1	9	118	123	40
9	1	0	93	109	16
9	1	1	45-	18	212
9	1	2	56	44	209
9	1	3	104	140	45
9	1	4	53	39	196
9	1	5	34-	33	277
9	1	6	74	113	40
9	1	7	14-	12	295
0	2	1	113	77	301
0	2	2	489	232	60
0	2	3	756	700	180
0	2	4	319	262	120
0	2	5	528	491	239
0	2	6	410	370	180
0	2	7	289	262	120
0	2	8	504	504	240
0	2	9	351	326	180
0	2	10	165	150	120
0	2	11	212	202	240
0	2	12	176	169	180
0	2	13	142	144	120
0	2	14	164	172	240
0	2	15	67	41	180
0	2	16	74	70	120
1	2	0	848	796	135
1	2	1	755	754	34
1	2	2	679	626	296
1	2	3	208	194	164
1	2	4	332	270	27
1	2	5	487	433	254
1	2	6	444	419	125
1	2	7	263	238	79
1	2	8	233	202	225
1	2	9	210	196	147
1	2	10	206	196	96
1	2	11	212	215	227
1	2	12	215	221	101
1	2	13	187	184	121
1	2	14	155	165	206
1	2	15	78	80	64
2	2	0	856	799	147
2	2	1	587	593	6
2	2	2	467	372	338
2	2	3	535	448	158
2	2	4	290	237	320
2	2	5	366	319	58
2	2	6	352	314	142
2	2	7	159	133	307
2	2	8	158	135	35
2	2	9	266	256	129
2	2	10	127	104	234
2	2	11	164	147	73
2	2	12	221	223	120
2	2	13	59-	26	212
2	2	14	51	36	135
2	2	15	71	87	98
3	2	0	361	354	311
3	2	1	464	449	9
3	2	2	322	279	358
3	2	3	494	440	308
3	2	4	488	451	328
3	2	5	289	259	22
3	2	6	268	231	291
3	2	7	471	462	342
3	2	8	287	278	38
3	2	9	127	130	281
3	2	10	203	203	340
3	2	11	150	148	62
3	2	12	115	112	294
3	2	13	112	118	18
3	2	14	38-	27	39
4	2	0	411	375	278
4	2	1	255	213	287
4	2	2	136	125	244
4	2	3	263	229	267
4	2	4	325	292	311
4	2	5	120	117	227
4	2	6	360	353	242
4	2	7	236	204	327
4	2	8	188	176	283
4	2	9	194	190	236
4	2	10	101	96	329
4	2	11	80	80	234
4	2	12	193	216	247
4	2	13	91	99	342
4	2	14	59	81	220
5	2	0	178	164	74
5	2	1	255	220	91
5	2	2	357	354	244
5	2	3	84	63	54
5	2	4	175	160	139
5	2	5	372	354	261
5	2	6	113	81	123
5	2	7	160	147	84
5	2	8	223	216	260
5	2	9	93	81	222
5	2	10	142	129	25
5	2	11	166	161	246
5	2	12	80	59	218
5	2	13	39	49	68
6	2	0	460	490	126
6	2	1	248	237	123
6	2	2	199	181	310
6	2	3	394	395	124
6	2	4	149	148	149
6	2	5	147	128	0
6	2	6	278	282	121
6	2	7	61	43	113
6	2	8	83	68	329
6	2	9	145	153	126
6	2	10	49	31	237
6	2	11	69	76	1
6	2	12	81	108	128
7	2	0	73-	45	76
7	2	1	195	180	48
7	2	2	156	155	352
7	2	3	110	107	62
7	2	4	106	115	36
7	2	5	156	165	20
7	2	6	138	121	47
7	2	7	84	83	15
7	2	8	125	126	30
7	2	9	81	76	349
7	2	10	81	101	333
8	2	0	80	88	264
8	2	1	57-	35	235
8	2	2	55-	41	158
8	2	3	53-	18	147
8	2	4	50-	20	234
8	2	5	46-	36	133
8	2	6	68	69	269
8	2	7	33-	36	290
8	2	8	20-	34	230
9	2	0	57	68	343
9	2	1	35-	36	148
9	2	2	81	100	200
9	2	3	46	56	2
0	3	1	870	817	120
0	3	2	447	339	60
0	3	3	466	373	180
0	3	4	538	516	120
0	3	5	466	413	60
0	3	6	658	623	180
0	3	7	705	749	120
0	3	8	151	144	60
0	3	9	417	426	180
0	3	10	289	296	120
0	3	11	85	63	60
0	3	12	190	185	180
0	3	13	241	244	120
0	3	14	94	78	60
0	3	15	29-	16	0
1	3	1	507	468	87
1	3	2	590	627	19
1	3	3	296	245	176
1	3	4	440	408	119
1	3	5	541	554	3
1	3	6	281	252	169
1	3	7	213	205	127
1	3	8	323	321	35
1	3	9	172	176	169
1	3	10	79	44	170
1	3	11	135	134	42
1	3	12	106	100	55
1	3	13	99	91	118
1	3	14	79	76	62
1	3	15	59	68	26
2	3	1	394	366	8
2	3	2	285	279	351
2	3	3	140	120	308
2	3	4	448	397	333
2	3	5	331	302	37
2	3	6	166	143	244
2	3	7	302	291	305
2	3	8	230	206	92
2	3	9	102	85	331
2	3	10	180	164	290
2	3	11	191	193	97
2	3	12	62	55	168
2	3	13	70	84	324
2	3	14	64	75	91
3	3	0	445	372	301
3	3	1	437	384	254
3	3	2	358	324	255
3	3	3	236	196	312
3	3	4	367	336	250
3	3	5	315	303	237
3	3	6	230	216	272
3	3	7	332	326	250
3	3	8	140	116	228
3	3	9	116	111	224
3	3	10	102	95	263
3	3	11	71	43	318
3	3	12	139	156	218
3	3	13	44	44	202
3	3	14	20-	30	252
4	3	0	67-	28	344
4	3	1	383	356	140
4	3	2	46-	11	149
4	3	3	91	85	276
4	3	4	157	143	149
4	3	5	74	43	154
4	3	6	214	202	214
4	3	7	181	173	90
4	3	8	80	70	22
4	3	9	184	178	193
4	3	10	177	186	99
4	3	11	47	55	102
4	3	12	165	174	198
4	3	13	94	125	110
5	3	0	92	39	57
5	3	1	252	242	120
5	3	2	325	330	330
5	3	3	138	122	286
5	3	4	210	196	114
5	3	5	329	326	324
5	3	6	82	86	358
5	3	7	237	237	118
5	3	8	202	222	327
5	3	9	75	57	282
5	3	10	125	126	97
5	3	11	88	106	322
5	3	12	20-	32	333
6	3	0	62	60	337
6	3	1	179	180	53
6	3	2	234	243	338
6	3	3	68	33	0
6	3	4	52	35	92
6	3	5	183	189	344
6	3	6	84	103	354
6	3	7	47-	30	34
6	3	8	85	93	333
6	3	9	85	87	327
6	3	10	71	80	266
7	3	0	53-	35	208
7	3	1	121	134	242
7	3	2	50-	68	286
7	3	3	47-	33	234
7	3	4	115	121	259
7	3	5	86	93	249
7	3	6	38-	25	337
7	3	7	129	148	241
7	3	8	61	99	263
8	3	0	35-	40	218
8	3	1	35-	66	72
8	3	2	124	157	113
8	3	3	32-	46	154
8	3	4	44	63	78
8	3	5	103	154	133
0	4	1	623	622	120
0	4	2	77	94	60
0	4	3	301	320	0
0	4	4	379	344	120
0	4	5	248	198	60
0	4	6	428	426	0
0	4	7	72	49	121
0	4	8	210	199	60
0	4	9	220	224	0
0	4	10	45-	2	297
0	4	11	43-	46	60
0	4	12	209	207	0
0	4	13	31-	30	300
0	4	14	75	85	60
1	4	1	374	362	193
1	4	2	267	260	340
1	4	3	90	75	121
1	4	4	395	389	226
1	4	5	94	85	34
1	4	6	169	145	69
1	4	7	390	405	226
1	4	8	153	156	66
1	4	9	129	135	167
1	4	10	254	255	238
1	4	11	61	50	44
1	4	12	82	77	102
1	4	13	167	170	257
1	4	14	57	56	51
2	4	1	269	229	202
2	4	2	184	155	158
2	4	3	78	37	58
2	4	4	102	100	237
2	4	5	169	142	131
2	4	6	182	181	205
2	4	7	139	130	217
2	4	8	135	115	132
2	4	9	86	66	228
2	4	10	78	52	152
2	4	11	142	134	120
2	4	12	92	97	202
2	4	13	39	21	279
2	4	14	62	97	19
3	4	0	45-	28	344
3	4	1	243	218	171
3	4	2	292	236	109
3	4	3	47-	20	0
3	4	4	80	71	165
3	4	5	142	125	146
3	4	6	45-	34	147
3	4	7	254	262	145
3	4	8	127	117	149
3	4	9	40-	28	147
3	4	10	135	128	129
3	4	11	126	143	114
3	4	12	85	89	169
3	4	13	73	113	137
4	4	0	332	373	339
4	4	1	45-	30	189
4	4	2	133	130	338
4	4	3	366	383	351
4	4	4	145	122	133
4	4	5	83	73	277
4	4	6	260	268	341
4	4	7	145	124	115
4	4	8	38-	34	325
4	4	9	111	136	356
4	4	10	97	92	104
4	4	11	22-	19	322
4	4	12	34	63	12
5	4	0	43-	17	40
5	4	1	115	128	226
5	4	2	116	106	314
5	4	3	86	82	265
5	4	4	131	140	236
5	4	5	153	132	306
5	4	6	100	93	313
5	4	7	102	122	215
5	4	8	71	75	320
5	4	9	27-	14	47
5	4	10	75	111	205
6	4	0	145	164	253
6	4	1	70	65	330
6	4	2	65	59	283
6	4	3	108	124	275
6	4	4	73	70	327
6	4	5	79	86	289
6	4	6	86	105	297
6	4	7	143	130	362
6	4	8	20-	17	140
6	4	9	50	58	340

Table 3 (*cont.*)

h	k	l	$10F_o$	$10F_c$	α°
7	4	0	81	86	190
7	4	1	27-	16	209
7	4	2	93	99	108
7	4	3	52	44	232
7	4	4	49	65	311
7	4	5	52	73	129
7	4	6	15-	43	215
0	5	1	60	47	120
0	5	2	584	590	240
0	5	3	77	77	0
0	5	4	355	314	120
0	5	5	277	258	240
0	5	6	145	149	0
0	5	7	125	112	120
0	5	8	199	219	239
0	5	9	200	182	0
0	5	10	60-	7	294
0	5	11	193	204	240
0	5	12	179	169	0
0	5	13	137	142	300
0	5	14	47	48	240
1	5	1	247	236	195
1	5	2	242	226	143
1	5	3	349	347	77
1	5	4	257	255	160
1	5	5	81	61	167
1	5	6	317	336	41
1	5	7	237	233	213
1	5	8	194	194	162
1	5	9	212	208	41
1	5	10	150	156	239
1	5	11	50-	46	110
1	5	12	108	115	49
1	5	13	123	133	257
2	5	1	426	421	234
2	5	2	179	162	143
2	5	3	259	223	52
2	5	4	300	275	225
2	5	5	251	219	145
2	5	6	234	217	80
2	5	7	226	225	230
2	5	8	178	174	161
2	5	9	116	105	49
2	5	10	123	135	214
2	5	11	61	41	34
2	5	12	44	28	120
2	5	13	55	66	223
3	5	1	180	176	339
3	5	2	360	358	127
3	5	3	92	58	138
3	5	4	164	170	24
3	5	5	259	262	126
3	5	6	86	60	135
3	5	7	124	112	63
3	5	8	108	101	150
3	5	9	70	62	153
3	5	10	120	128	73
3	5	11	78	86	115
3	5	12	60	71	158
4	5	0	63-	17	40
4	5	1	120	127	2
4	5	2	118	126	240
4	5	3	95	85	274
4	5	4	123	123	96
4	5	5	137	144	259
4	5	6	92	87	335
4	5	7	139	137	83
4	5	8	66	78	251
4	5	9	64	64	63
4	5	10	116	142	103
5	5	0	101	62	284
5	5	1	105	101	317
5	5	2	55	53	346
5	5	3	60	45	316
5	5	4	68	78	316
5	5	5	63	59	352
5	5	6	71	68	352
5	5	7	57	54	292
5	5	8	41	37	46
5	5	9	44	68	45
6	5	0	56	69	254
6	5	1	118	190	262
6	5	2	40-	32	192
6	5	3	51	68	277
6	5	4	175	203	265
6	5	5	95	68	244
6	5	6	37	58	272
0	6	1	70	95	120
0	6	2	182	169	240
0	6	3	50-	11	0
0	6	4	51-	8	300
0	6	5	298	295	240
0	6	6	97	85	0
0	6	7	91	100	300
0	6	8	172	170	240
0	6	9	121	123	0
0	6	10	45-	25	301
0	6	11	149	178	240
0	6	12	91	89	0
0	6	13	118	133	300
1	6	0	238	226	129
1	6	1	149	125	313
1	6	2	386	387	208
1	6	3	216	223	108
1	6	4	94	86	329
1	6	5	336	332	213
1	6	6	260	265	72
1	6	7	80	72	105
1	6	8	258	280	224
1	6	9	110	99	33
1	6	10	40-	29	286
1	6	11	161	178	243
1	6	12	60	50	56
2	6	1	53-	41	341
2	6	2	222	216	118
2	6	3	358	395	111
2	6	4	80	82	158
2	6	5	106	99	117
2	6	6	301	323	119
2	6	7	89	81	105
2	6	8	44-	45	135
2	6	9	181	193	123
2	6	10	51	52	158
2	6	11	64	58	259
3	6	1	176	169	4
3	6	2	140	159	54
3	6	3	93	65	254
3	6	4	192	206	38
3	6	5	211	232	68
3	6	6	60	28	240
3	6	7	183	191	41
3	6	8	124	119	40
3	6	9	31-	15	238
3	6	10	84	101	32
4	6	1	84	102	1
4	6	2	45-	17	54
4	6	3	84	89	228
4	6	4	68	82	56
4	6	5	38-	20	60
4	6	6	104	114	248
4	6	7	57	44	320
4	6	8	25-	3	33
4	6	9	16-	27	239
5	6	0	77	69	254
5	6	1	35-	18	304
5	6	2	161	199	233
5	6	3	53	38	214
5	6	4	44	39	296
5	6	5	115	133	222
5	6	6	22-	18	212
0	7	1	103	76	120
0	7	2	73-	7	56
0	7	3	133	99	180
0	7	4	114	145	121
0	7	5	73	44	240
0	7	6	93	80	180
0	7	7	63-	30	120
0	7	8	60-	14	241
0	7	9	64	66	180
0	7	10	44-	11	121
0	7	11	45	42	240
0	7	12	22-	13	180
1	7	1	190	192	110
1	7	2	131	117	47
1	7	3	89	87	150
1	7	4	70-	21	106
1	7	5	68-	55	32
1	7	6	97	92	122
1	7	7	84	93	72
1	7	8	68	49	4
1	7	9	46-	20	13
1	7	10	46	50	127
1	7	11	72	97	332
2	7	1	227	248	9
2	7	2	161	152	46
2	7	3	70-	20	154
2	7	4	105	125	7
2	7	5	161	171	44
2	7	6	59-	50	98
2	7	7	121	130	0
2	7	8	112	118	12
2	7	9	48	48	238
2	7	10	26-	62	335
3	7	1	53-	19	270
3	7	2	61	90	264
3	7	3	70	91	202
3	7	4	47-	43	227
3	7	5	44-	2	225
3	7	6	103	134	213
3	7	7	32-	26	270
3	7	8	26-	72	296
3	7	9	90	71	284
4	7	1	70	79	99
4	7	2	27-	46	113
4	7	3	70	119	177
4	7	4	63	106	94
4	7	5	47	72	93
4	7	6	70	105	170
0	8	1	66-	55	301
0	8	2	66-	62	60
0	8	3	193	197	0
0	8	4	167	166	300
0	8	5	77	72	240
0	8	6	157	193	0
0	8	7	77	96	300
0	8	8	62	73	60
0	8	9	104	109	0
0	8	10	28-	44	300
1	8	1	99	113	242
1	8	2	68	58	357
1	8	3	60-	56	50
1	8	4	160	189	263
1	8	5	91	91	4
1	8	6	49-	36	179
1	8	7	104	126	273
1	8	8	86	95	8
1	8	9	40	62	213
2	8	1	57-	36	137
2	8	2	73	61	8
2	8	3	134	168	239
2	8	4	50-	20	87
2	8	5	83	90	7
2	8	6	143	177	237
2	8	7	33-	26	67
2	8	8	20-	62	12
3	8	1	112	188	125
3	8	2	41	66	22
3	8	3	38	46	183
3	8	4	94	135	117
3	8	5	52	88	53
0	9	1	53-	4	117
0	9	2	139	140	240
0	9	3	73	42	0
0	9	4	47-	27	299
0	9	5	89	125	240
0	9	6	70	52	0
0	9	7	60	56	300
0	9	8	31	57	239
1	9	1	68	49	250
1	9	2	59	55	352
1	9	3	72	91	356
1	9	4	86	92	247
1	9	5	62	80	350
1	9	6	40	61	357
2	9	1	116	144	218
2	9	2	33-	14	99
2	9	3	36	53	310
0	10	1	89	79	301
0	10	2	79	81	240
0	10	3	78	78	0
0	10	4	26-	25	299

Experimental

The crystals of Ni*tam*$_2$(NCS)$_2$ used in the present work were those already described by Nardelli & Chierici (1958). Cell constants, remeasured and refined by a least-squares procedure on powder diffractometer data (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å), are as follows:

$$\mathrm{Ni[SC(CH_3)NH_2]_2(NCS)_2},\ M = 325{\cdot}1$$

$$a = 9{\cdot}463 \pm 0{\cdot}009,\ c = 12{\cdot}627 \pm 0{\cdot}022\ \text{Å},$$

$$V = 979\ \text{Å}^3,\ Z = 3,\ D_x = 1{\cdot}66,\ D_m = 1{\cdot}63\ \mathrm{g.cm^{-3}}$$

$$\mu = 78{\cdot}7\ \mathrm{cm^{-1}}\ (\mathrm{Cu}\ K\alpha)$$

Space groups: $P3_121$ or $P3_221$.

Three-dimensional intensity data were recorded in the usual way on multiple-film Weissenberg photographs, using integration and equi-inclination techniques with Cu $K\alpha$ radiation, and the intensities were measured photometrically. Layers *h*0.*l* to *h*6.*l* were recorded about the *b* axis giving all the possible reflexions (857 independent ones) which lie within the limiting sphere for Cu $K\alpha$; of these, 127 were too weak to be estimated.

To correct for absorption the sample was treated as a sphere of mean radius 0·047 cm. The structure factors were derived by the usual formulae, the absolute scale being established by Wilson's method using the *h*0.*l* reflexions; the remaining layers were put on the same absolute scale by comparison of the symmetry related reflexions which occur in both the *n* and the zero layer.

Structure analysis and refinement

The centre of mass of the three molecules in the unit cell must be found in one of the two positions, (*a*) or (*b*), of three points lying on a binary axis in the two possible space-groups, $P3_121$ and $P3_221$. As these groups are enantiomorphous it is possible to select either: the space-group $P3_121$ was chosen. The coordinates of Ni, S(1) and S(2) were first found from a three-dimensional Patterson synthesis. The next step was a three-dimensional Fourier synthesis calculated with the use of the phases of the contributions of these atoms to the structure factors ($R = 36\%$); this synthesis showed all the other atoms to be well resolved. Two more three-dimensional Fourier calculations, followed by an $F_o - F_{\mathrm{Ni}}$ synthesis, improved the residual error index to 22%. The refinement was then carried out by means of seven cycles of Booth's differential synthesis, two calculated with isotropic and five with anisotropic thermal parameters. The final agreement indices were: $R = 10{\cdot}8\%$, $R' = 12{\cdot}9\%$ (R, for observed reflexions only; R' assuming $F_o = \frac{1}{2}F_{\min}$ when $F_c > F_{\min}$ for unobserved reflexions, multiplicities not considered).

At the end of this refinement, the ratios $r(x) = |\sigma(x)/\varepsilon(x)|$ between the e.s.d.'s and the shifts of the coordinates were as shown in Table 1, in which the final parameters with their e.s.d.'s (Cruickshank, 1949, 1956) are also quoted. The B_{ij}'s were determined by the method of Nardelli & Fava (1960) using the second derivatives of the electron density in the differential synthesis.* Observed and calculated peak heights and curvatures, with the e.s.d.'s of electron-density and second derivatives, are reported in Table 2. The F_c

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* The method used to determine the matrix elements of tensor **B** is based on the electron density distribution; therefore the symmetry relations on the B_{ij} values must derive directly with no imposed restriction. This is observed for Ni, which is in the (*a*) position of the $P3_121$ space group: in fact the relations $B_{22} = 2B_{12}$ and $B_{23} = 2B_{13}$ required by the space group symmetry are well verified in the limits of the e.s.d.'s.

values reported in Table 3 are calculated with the final parameters of Table 1 using the scattering factors of Thomas & Umeda (1957) for Ni^{2+}, of Dawson (1960) for S and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for N and C.

The standard deviations, quoted in the next section, are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles, the effects of errors in cell parameters being accounted for following Darlow & Cochran (1961).

Discussion

The coordination around each nickel atom is octahedral as it coordinates to two S(1) atoms from two thioacetamide molecules and to two S(2) and two N(2) atoms from four different NCS groups. The structure is polymeric as these groups are in a bridging position and the coordination octahedra form a helical chain running around a 3_1 axis as shown in Fig. 1. The two thioacetamide molecules are in a *cis* position, their sulphur atoms being on adjacent corners of the coordination octahedron.

It is interesting to compare this structure with those of the similar compounds Ni*etu*$_2$(NCS)$_2$ (Nardelli, Fava Gasparri, Musatti & Manfredotti, 1966) and Ni*tu*$_2$(NCS)$_2$ (Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966) complexes (Fig. 2). In all these three compounds coordination around Ni is octahedral and the crystal structures are polymeric in nature with chains of coordination polyhedra; however, while sulphur bridges are present in the thiourea complex, bridging is due to the thiocyanate groups in the other compounds. The ligands are in a different

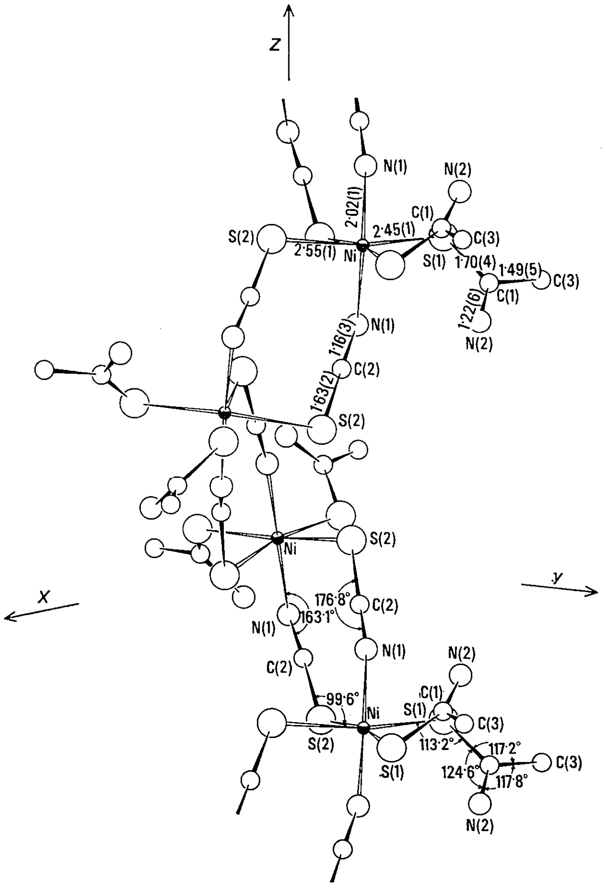

Fig. 1. Ni*tam*$_2$(NCS)$_2$: Clinographic projection of a chain of coordination polyhedra.

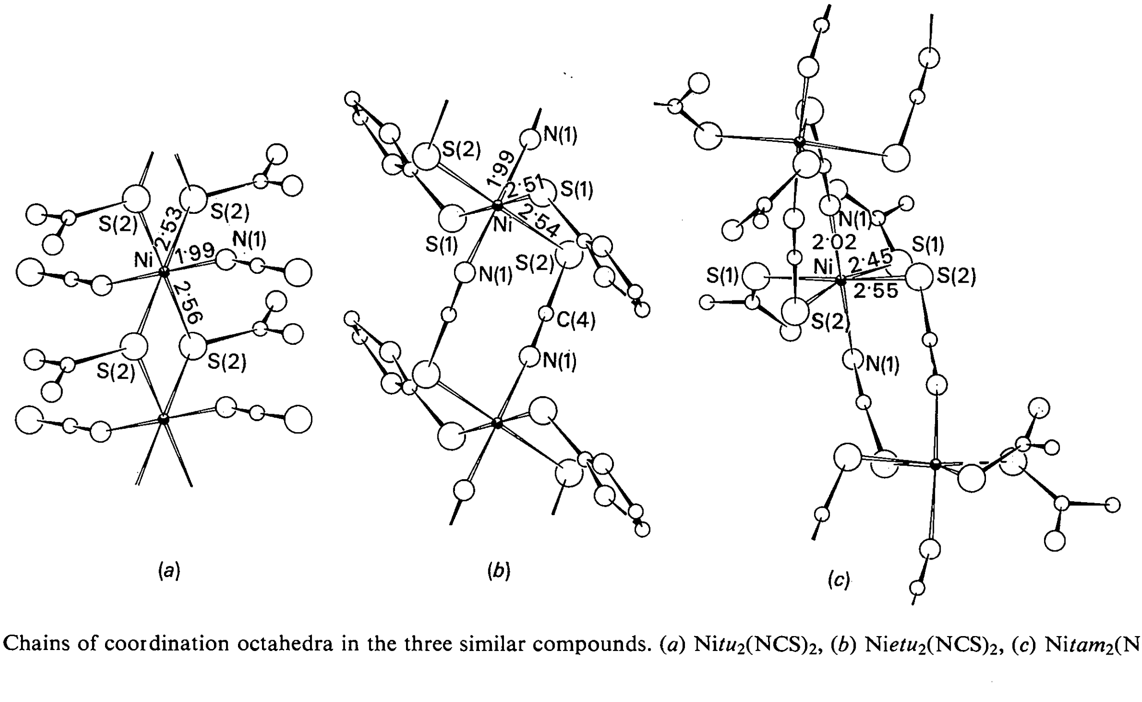

Fig. 2. Chains of coordination octahedra in the three similar compounds. (*a*) Ni*tu*$_2$(NCS)$_2$, (*b*) Ni*etu*$_2$(NCS)$_2$, (*c*) Ni*tam*$_2$(NCS)$_2$.

situation in the three complexes: in Ni*tu*$_2$(NCS)$_2$ the thiocyanate is terminal and bonded through the nitrogen atom and each sulphur atom of thiourea is bonded to two adjacent metal atoms, while in Ni*etu*$_2$(NCS)$_2$ the thiocyanate group is bridging and the two ethylenethiourea sulphur atoms, which are monocoordinated, are in a *trans* position.

It is remarkable to observe that in all these compounds coordination always involves four sulphur and two nitrogen atoms, the last being *trans* with respect to the sulphur plane, so that the octahedra are deformed to form flattened bipyramids which are nearly tetragonal. Thus this polyhedron seems to be the most stable arrangement for the Ni^{2+} ion with these ligands and is realized in different ways, with different behaviour of the thiocyanate group. This behaviour is probably related to the different donor character of the ligands and to the packing interactions of the organic molecules.

Comparison of bond distances and angles in the coordination polyhedra of the three nickel thiocyanate complexes is shown in Table 4. The distances Ni–S for the two kinds of coordinated sulphur atom in the thioacetamide complex are significantly different [$t_o=(l_1-l_2)\times(\sigma_1^2+\sigma_2^2)^{-1/2}=7{\cdot}1$, significance test of Cruickshank & Robertson, 1953], the shorter being

Table 4. *Bond distances and angles in the coordination octahedra of* Ni*L*$_2$(NCS)$_2$ *complexes*

[*L* = thioacetamide (*tam*), ethylenethiourea (*etu*), thiourea (*tu*)]

	Ni*tam*$_2$(NCS)$_2$*	Ni*etu*$_2$(NCS)$_2$†	Ni*tu*$_2$(NCS)$_2$‡
Ni–S(1)	2·446 ± 10 Å	2·507 ± 8 Å	2·531 ± 6 Å
Ni–S(2)	2·546 ± 10	2·544 ± 14	2·564 ± 9
Ni–N(1)	2·020 ± 11	1·992 ± 23	1·992 ± 7
N(1)–Ni–S(2^{i})	92·6 ± 1·0°	88·0 ± 0·5°	82·4 ± 0·3°
N(1)–Ni–S(2^{ii})	85·5 ± 0·9		
S(1) –Ni–S(1^{iii})	101·5 ± 0·3	81·4 ± 0·2	83·6 ± 0·1
S(1) –Ni–S(2^{i})	87·4 ± 0·4		
S(1) –Ni–N(1)	86·9 ± 0·9	87·3 ± 0·5	88·3 ± 0·3
S(1) –Ni–N(1^{iii})	94·7 ± 0·9		

* Present paper.
† Nardelli, Fava Gasparri, Musatti & Manfredotti (1966).
‡ Nardelli, Fava Gasparri, Giraldi Battistini & Domiano (1966).

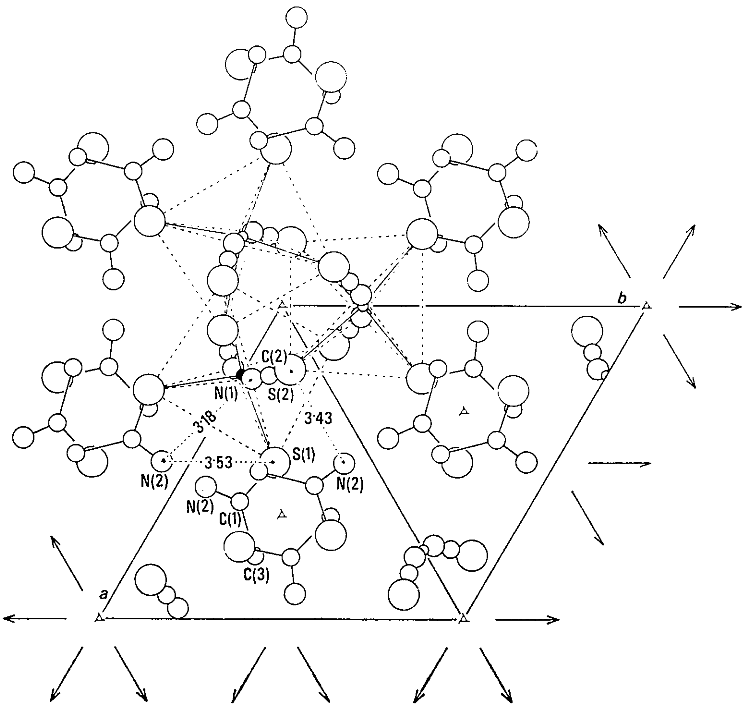

Fig. 3. Ni*tam*$_2$(NCS)$_2$: projection of the structure on a plane perpendicular to [001].

that of the thioacetamide sulphur which is more strongly bonded to the metal atom than the other sulphur ligand. The distance Ni–N is consistent with the sum of Pauling's covalent radii (2·09 Å) and with the data quoted in Table 4 of the paper on bis(2-thioimidazolidine)nickel(II) thiocyanate (Nardelli, Fava Gasparri, Musatti & Manfredotti, 1966).

Distances and angles in the thioacetamide molecule are compared with those for the uncoordinated molecule (Truter, 1960) in Table 5. From these values it appears that coordination does not significantly influence the dimensions of the molecule, which is planar; its least-squares plane is

$$0\cdot1893X-0\cdot6519Y+0\cdot7343Z=3\cdot9141\ .^{*}$$

The thioacetamide molecule is tilted with respect to the plane of sulphur atoms surrounding the nickel atom, the dihedral angle being 132·0° (the values for the same angle in the thiourea and ethylenethiourea complexes are 100·2° and 107·1° respectively). This is a consequence of the lack of collinearity for the bonds Ni–S(1) and S(1)–C(1): the angle Ni–S(1)–C(1) being 113·2° (116·9° for the *tu* complex and 116·9° for the *etu* complex).

Table 5. *Distances and angles in thioacetamide molecules*

Ni*tam*$_2$(NCS)$_2$ (Present study)	*tam* (Truter, 1960)	t_o
S(1)–C(1) = 1·70 ± 4	1·713 ± 6	0·32
C(1)–C(3) = 1·49 ± 5	1·494 ± 8	0·08
C(1)–N(2) = 1·22 ± 6	1·324 ± 8	1·72
S(1)–C(1)–N(2) = 124·6 ± 3·2°	121·6 ± 0·4°	0·93
S(1)–C(1)–C(3) = 117·2 ± 3·3	120·7 ± 0·4	1·06
N(2)–C(1)–C(3) = 117·8 ± 3·3	117·7 ± 0·5	0·03

Table 6. *Distances and angles in the NCS group*

	Ni*etu*$_2$(NCS)	Ni*tu*$_2$(NCS)$_2$	Ni*tam*$_2$(NCS)$_2$
N–C	1·16 ± 3 Å	1·169 ± 14 Å	1·16 ± 3 Å
C–S	1·64 ± 2	1·635 ± 13	1·63 ± 2
Ni–N–C	162·1 ± 1·7°	162·2 ± 1·0°	163·1 ± 3·2°
Ni–S–C	100·7 ± 0·7	—	99·6 ± 1·5
N–C–S	178·6 ± 1·2	178·0 ± 1·0	176·8 ± 3·8

The bond distances and angles concerning the NCS group are practically equal in the three nickel complexes, as shown in Table 6, so that the discussion given for the NCS group in the *etu* complex (Nardelli, Fava Gasparri, Musatti & Manfredotti, 1966) applies also to the other two complexes. The lack of collinearity in the NCS group is not significant. The infrared behaviour of this group in these complexes is illustrated in the paper describing the crystal structure of the *etu* complex.

Packing is determined by the following S···N and N···N contacts:

$$S(2)\text{–}N(2^{iv})=3\cdot43\pm4\ \text{Å}$$
$$N(1)\text{–}N(2^{iii})=3\cdot18\pm6$$
$$S(1)\text{–}N(1^{iii})=3\cdot29\pm3$$

i $x, y, 1-z$
ii $y-x, \bar{x}, z-\frac{1}{3}$
iii $x-y, \bar{y}, \frac{2}{3}-z$
iv $y-x+1, 1-x, \frac{2}{3}+z$

as shown in the projection of Fig. 3.

All the calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico della Università di Parma with the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965). This work was done with the financial support of the Consiglio Nazionale delle Ricerche (Roma).

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* The X, Y, Z coordinates are in Å and refer to orthogonal axes. They can be obtained from those of Table 1 by using the matrix:

$$\begin{pmatrix} a\sin\gamma & 0 & 0 \\ a\cos\gamma & b & 0 \\ 0 & 0 & c \end{pmatrix}.$$