Acta Cryst. (1972). **B28**, 2640

The Crystal and Molecular Structure of *trans*-Dichlorotetrakis(thioacetamide)Ni(II)

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(*Received* 13 *April* 1972)

The crystal structure of *trans*-dichlorotetrakis(thioacetamide)Ni(II) has been determined from 3005 intensities measured at room temperature using counter techniques and refined by full-matrix least-squares to a final R of 0·034. The space group is $P\bar{1}$, $Z=2$, $d_m=1{\cdot}55$, $d_c=1{\cdot}55$ g.cm^{-3} with $a=13{\cdot}501$ (5), $b=9{\cdot}581$ (6), $c=9{\cdot}880$ (7) Å, $\alpha=90{\cdot}8$ (1), $\beta=134{\cdot}4$ (1), $\gamma=90{\cdot}8$ (1)°. There are two crystallographically independent molecules per cell with the Ni atoms on centers of symmetry demanding the *trans* configuration, equal Ni–Cl distances within the molecule and coplanarity of the Ni and its four sulfur nearest neighbors. The two independent Ni–Cl distances are 2·427 (1) and 2·430 (1) Å. The four independent Ni–S distances are 2·460 (1), 2·466 (1), 2·458 (1) and 2·459 (1) Å. The thioacetamide molecules (excluding hydrogen atoms) are planar. Only normal van der Waals distances are found between molecules. The S–C, C–N and C–C distances are within one standard deviation (±0·004, ±0·006, ±0·006) of the average of the four independent distances of 1·679, 1·307 and 1·502 Å respectively.

Introduction

Thiourea (tu) has several possible modes of binding to transition metals: (1) *via* the nitrogen atom, that is behaving as a N-donor, which has never been observed; (2) binding through the sulfur lone-pair orbitals. The latter mode seems to be the most common and has been shown to exist by a number of structure determinations of thiourea and thiourea-derivatives complexed with transition metals (Berta, Spofford, Boldrini & Amma, 1970; O'Connor & Amma, 1969; Weininger, O'Connor & Amma, 1969; Spofford, Boldrini, Amma, Carfagno & Gentile, 1970; Nardelli, Gasparri, Battistini & Domiano, 1966; Lopez-Castro & Truter, 1963; Gasparri, Mangia, Musatti & Nardelli, 1969; Sirigu, 1969; Nardelli, Gasparri, Musatti & Manfredotti, 1966; Robinson, Holt & Carpenter, 1967; Lüth & Truter, 1968.) The third possibility is *via* the sulfur–carbon π-orbitals. This has been observed in $Cotu_4(NO_3)_2$ and $Cotu_4(NO_3)_2.2H_2O$ (Spofford, Boldrini, Amma, Carfagno & Gentile, 1970). The color and, consequently, the spectra of $Nitu_4Cl_2$ and also of $NiCl_2$ with derivatives of thiourea, are quite interesting; for example, *trans*-$Nitu_4Cl_2$ is olive green with two distinctly different Ni–Cl distances of 2·40 (2) and 2·52 (2) Å (Lopez-Castro & Truter, 1963). This particular structure has an umbrella-like arrangement with a real fourfold axis and the thiourea groups tipped toward one of the apical chlorines. Somewhat surprisingly the thiourea groups are tipped toward, and hydrogen bonded to, the chlorine belonging to the shortest Ni–Cl distance. This compound was once thought to be representative of the entire series of transition metal thiourea complexes with the same structure, *i.e.* where the metal was Ni, Co, Mg, Fe and Cd (Cavalca, Nardelli & Braibanti, 1956). However, we have shown in an earlier publication that *trans*-$Nitu_4Cl_2$ is unique and the other members of this series have equal metal–chlorine distances (O'Connor & Amma, 1969). In fact, in all of these cases the metal sits on a center of symmetry. However, *trans*-dichlorotetrakis(ethylenethiourea) Ni(II) is polymorphic, crystallizing in two forms, both of which have been shown to have Ni(II) coordinated to 4S and 2Cl in a *trans* arrangement (Robinson, Holt & Carpenter, 1967). Lüth & Truter (1968) found in dichlorotetrakis(trimethylenethiourea)Ni(II) that again the coordination polyhedron is made up of four sulfur atoms and two chlorine atoms in a *trans* octahedral geometry. In all of these cases the metal is bound to the sulfur by what appears to be a non-bonding sp^2 lobe of the sulfur atom.

Nardelli & Chierici (1957) have reported the preparation of $M(tac)_2Cl_2$ where M = iron, cobalt, zinc or cadmium and tac = thioacetamide. The electronic and vibrational spectra of $M(tac)_2X_2$ were reported by Flint & Goodgame (1968), where M is as above and M′ = Ni, Pd, Pt and Cd, and X = Cl or Br. Nardelli & Chierici (1958) also reported the preparation of a complex having the stoichiometry $M(tac)_4Cl_2$, where M = Ni or Cd. The only other crystal structures of transition metal complexes with thioacetamide thus far reported are those of bis(thioacetamide)Ni(II) thiocyanate (Capacchi, Gasparri, Nardelli & Pelizzi, 1968) and tetrakis(thioacetamide)Ni(II) bromide (Spofford, Boldrini & Amma, 1971).

Experimental

Dichlorotetrakis(thioacetamide)nickel(II), $Ni(tac)_4Cl_2$, was prepared as follows: 3 g (0·038 mole) powdered thioacetamide were added with constant stirring to 25 ml of hot ethanol in which 2 g (~0·01 mole) of $NiCl_2.6H_2O$ had been dissolved. The crude product

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[*] Partial fulfillment for the Ph.D. requirements at the University of South Carolina, 1969.

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Table 1 (*a*). *Observed and calculated structure factors*

First column is *h* followed by 10*F*(obs) and 10*F*(calc) on an absolute scale. Reflections denoted by a negative *F*(obs) were not used in the refinement.

H K=	0 L=	0
4	571	600
7	52	44
8	73	67
9	69	57
10	89	-92
11	53	52
12	88	88
H K=	1 L=	0
-2	45	36
-3	168	165
3	383	381
-4	68	68
4	84	-84
-5	140	126
5	234	225
-6	87	86
6	67	-62
7	44	42
-7	62	52
8	43	-38
-8	50	46
9	70	-67
-9	119	121
-10	44	44
-11	45	48
-13	62	64
H K=	2 L=	0
0	159	132
1	105	-112
-1	75	70
-2	77	-83
3	71	-66
-3	89	-75
4	332	329
-4	355	347
5	102	-100
-5	164	-167
6	89	-87
-6	123	-118
7	121	-117
-7	131	-132
-8	238	233
8	179	167
9	56	-56
-9	73	-71
12	83	85
-12	99	102
H K=	3 L=	0
-2	175	-172
2	178	180
-3	151	153
3	284	291
4	270	273
-4	307	-304
-5	243	235
5	62	-65
-6	254	-249
6	105	106
-7	78	77
7	100	94
8	44	46
-8	101	-98
-9	122	120
11	64	65
-12	43	39
-13	49	48
H K=	4 L=	0
-1	133	-123
1	204	206
-2	266	246
2	152	160
-3	199	-187
3	189	192
4	310	313
-4	375	370
-5	102	-100
5	179	174
-6	163	166
-7	63	-64
7	91	86
8	100	96
-8	192	188
10	41	-37
-11	53	57
12	73	70
-12	83	87
H K=	5 L=	0
1	55	63
-1	268	279
2	99	99
-2	89	-88
3	268	288
-3	57	-53
-5	224	219
5	115	115
6	62	62
7	164	165
-7	54	56
-9	171	174
10	57	-54
-11	56	58
11	50	48
H K=	6 L=	0
0	92	77
-2	56	-64
-3	39	-32
4	147	153
-4	121	115
-5	106	-107
-6	60	64
-7	51	-52
8	134	131
-8	132	132
-9	44	-48
9	41	-39
-10	74	79
12	55	53
-12	67	73
H K=	7 L=	0
1	50	-50
-1	131	125
2	124	132
3	170	171
4	193	201
-4	125	-123
-5	170	168
-6	107	-104
6	74	77
7	133	139
-8	44	-43
-9	157	162
11	83	84
H K=	8 L=	0
0	96	94
2	78	81
-2	80	83
3	43	46
-4	123	123
4	129	135
5	55	53
-5	77	79
-6	112	112
6	85	87
7	40	35
-7	45	49
-8	129	121
8	74	78
-10	52	57
H K=	9 L=	0
-1	89	93
2	63	-62
3	141	144
9	86	87
H K=	-7 L=	1
0	248	243
-1	137	130
-2	57	57
2	154	151
-3	190	194
3	135	-130
4	160	151
-4	125	132
5	169	-161
-5	162	168
6	116	118
-6	45	44
7	76	-77
-7	57	60
8	90	88
H K=	-6 L=	1
0	43	42
1	290	289
-2	43	34
2	105	-101
-3	160	165
4	172	-165
5	197	194
-5	61	-66
6	215	-217
-6	45	-51
-7	95	94
8	82	-80
9	99	100
-11	64	66
H K=	-5 L=	1
0	184	183
1	41	-35
-2	130	134
-3	162	-171
3	73	67
-4	180	182
4	217	208
5	52	52
-5	123	-126
-6	38	-35
-7	81	-79
-8	85	84
8	105	101
-10	41	-43
12	76	81
H K=	-4 L=	1
0	65	57
-1	307	301
1	562	575
-2	37	-38
2	64	[illegible]
4	111	106
-4	46	-44
-5	61	63
5	262	247
-6	52	-50
6	53	49
-7	87	83
-9	60	-59
9	92	97
10	47	48
-11	47	49
13	50	55
H K=	-3 L=	1
0	826	848
1	54	47
-2	140	151
-3	36	40
-4	323	324
4	413	408
-5	99	87
5	79	-71
8	97	94
-8	89	91
-9	81	81
10	90	-90
-12	108	111
H K=	-2 L=	1
0	44	-46
-2	231	-241
-3	265	247
3	174	156
4	95	-89
-4	85	-90
5	215	206
-5	84	81
-6	148	-139
6	38	-39
-7	140	133
-8	54	-57
-9	61	61
9	41	38
10	69	-73
-11	91	91
13	52	59
H K=	-1 L=	1
2	65	-74
-3	369	-358
3	339	325
4	429	428
-4	389	380
5	205	206
-5	242	-240
6	43	-38
7	160	149
-7	140	-116
-8	253	241
8	164	163
-9	41	-42
12	103	106
-12	80	82
-13	45	44
H K=	0 L=	1
-3	369	365
3	308	306
4	278	276
5	217	207
-5	203	193
6	92	93
-6	39	-32
7	70	66
-7	144	142
8	61	58
-9	89	92
9	39	41
-11	56	59
13	44	41
H K=	1 L=	1
-1	71	-57
3	216	208
-3	230	-215
-4	355	342
4	421	416
5	81	77
-5	32	-27
-6	60	60
-7	69	-63
-8	324	322
8	140	135
-9	75	75
-10	81	82
10	80	-79
12	67	71
-12	147	153
H K=	2 L=	1
0	38	44
-1	171	-193
-2	277	-285
2	221	238
3	124	120
-2	54	-50
-3	103	96
-4	157	151
4	274	278
-5	151	147
-6	72	70
6	112	111
7	41	-36
-7	109	108
-8	198	204
8	132	132
-10	79	81
-12	94	100
12	52	53
H K=	6 L=	1
0	50	-45
-1	73	-64
1	213	-210
2	114	-117
-2	79	75
3	121	122
-3	113	-103
4	144	-149
-4	128	126
-5	131	131
6	75	-76
-6	119	118
7	196	199
8	42	-42
-9	176	180
9	57	58
11	82	86
H K=	7 L=	1
0	56	57
2	44	49
-2	37	38
-4	166	163
4	93	93
-6	67	69
6	61	61
6	64	61
-7	44	-43
8	134	135
-8	107	108
10	61	65
H K=	8 L=	1
-1	215	207
-2	37	31
-3	41	38
3	169	174
-5	179	174
6	42	41
-6	63	65
7	153	157
-8	56	49
-9	59	63
H K=	9 L=	1
0	137	135
1	72	-74
-2	118	117
2	73	73
3	107	-109
-3	69	69
4	97	100
-4	64	65
-5	100	99
5	77	-73
-6	44	48
6	83	80
-7	74	75
8	44	49
H K=	10 L=	1
-1	74	77
2	56	-57
3	61	63
4	69	-67
-5	50	54
7	53	57
H K=	11 L=	1
0	47	47
-2	79	80
2	58	57
-4	69	68
-6	44	47
H K=	12 L=	1
-1	134	125
1	65	66
3	78	80
-3	69	71
-5	81	81
H K=	13 L=	1
0	61	61
2	60	60
H K=	-12 L=	2
0	86	85
2	98	98
-2	93	97
4	56	57
6	50	55
H K=	-11 L=	2
0	45	44
1	129	131
-1	56	52
3	67	66
-3	88	91
-4	63	65
5	88	92
H K=	-10 L=	2
0	46	52
-2	56	53
2	76	78
-3	60	53
3	50	-45
5	64	-68
6	43	46
7	59	-66
H K=	-9 L=	2
1	165	160
-1	37	34
-2	41	-39
-3	113	113
5	97	98
-6	66	-65
-7	49	49
9	62	64
H K=	-8 L=	2
0	276	274
-2	186	187
2	225	231
-3	57	-60
4	179	181
-4	91	91
6	67	67
H K=	-7 L=	2
0	70	72
1	300	288
-1	67	58
2	81	-81
3	108	102
-3	171	173
4	48	53
5	221	217
-7	100	103
9	44	45
-11	75	75
H K=	-6 L=	2
0	161	156
2	58	57
-2	39	40
-3	63	-57
-4	104	107
4	109	103
-5	64	-59
-7	80	-71
7	37	-34
-8	294	292
8	170	166
9	82	-82
-10	91	91
12	101	105
-12	128	129
H K=	-1 L=	2
1	183	-210
2	239	229
-2	309	-307
3	28	-34
-4	240	-231
4	274	265
5	149	149
-5	151	152
-6	214	-207
6	104	99
7	147	144
-7	313	303
-8	103	-99
8	40	37
9	172	173
-9	207	200
-11	87	89
11	96	98
13	82	85
H K=	0 L=	2
1	28	-24
-1	64	61
3	269	267
-3	71	-74
4	431	443
-4	512	523
-5	103	101
5	169	172
-6	75	73
6	39	42
7	201	197
-8	288	276
8	363	361
-9	62	58
9	45	48
10	66	71
-12	80	84
12	117	118
H K=	1 L=	2
-1	427	444
1	396	408
-2	97	96
2	74	-74
-3	158	152
3	393	387
-4	129	128
4	53	-49
5	244	240
-5	236	227
-6	142	139
7	222	218
-7	138	134
-8	87	84
9	139	142
-9	96	96
-11	92	93
11	62	61
-13	55	62
H K=	2 L=	2
-1	84	85
1	69	-74
2	407	-418
-2	472	-482
-3	66	66
3	38	-44
-4	106	108
4	270	271
5	147	-145
-5	219	213
-6	71	70
6	122	122
-8	227	224
8	256	254
9	95	-91
10	49	47
-10	54	55
-11	70	-75
12	107	112
-12	120	124
H K=	3 L=	2
-1	80	82
1	138	-143
-2	123	115
2	61	-59
3	47	53
-4	72	66
4	152	-152
-5	218	216
5	123	120
-6	58	50
7	241	235
-7	79	79
-8	63	-63
9	132	132
-9	143	147
-10	67	-66
11	141	145
-12	58	-62
H K=	4 L=	2
0	310	320
-1	141	132
1	165	-161
2	123	126
-2	175	176
-3	93	89
4	257	262
-4	396	399
-5	118	123
-7	66	71
7	56	59
8	193	189
-8	150	148
9	55	55
-9	45	51
11	56	56
12	82	85
-12	48	48
H K=	5 L=	2
0	99	-97
1	174	183
-1	370	377
2	133	-135
-2	154	153
3	316	335
-3	171	166
4	148	-155
-4	129	131
5	55	49
-5	220	216
6	103	-105
-6	178	174
7	152	147
-8	70	69
8	46	-36
-9	86	87
-10	57	56
10	51	49
11	58	62
H K=	6 L=	2
0	124	118
1	67	-69
-3	54	53
3	147	-152
4	117	161
5	69	64
H K=	-11 L=	3
0	101	104
2	145	146
-2	82	85
4	109	108
6	57	60
H K=	-10 L=	3
1	68	74
-1	46	-39
-2	42	-39
-3	46	48
5	72	76
6	47	-47
-7	60	63
H K=	-9 L=	3
-1	63	-64
-3	107	-107
3	43	46
-4	42	43
-5	105	-111
5	55	60
-6	59	62
6	52	54
-7	56	-59
H K=	-8 L=	3
1	219	208
-1	106	108
-2	128	-124
-3	196	193
3	54	50
-4	46	-44
4	164	164
5	123	124
6	80	79
-6	70	-72
-7	89	96
8	99	100
9	61	68
H K=	-7 L=	3
0	213	207
2	210	208
-2	190	184
3	89	85
-3	63	-63
4	244	242
-4	136	136
5	104	102
-6	73	74
6	60	64
7	67	67
-8	104	[illegible]
8	[illegible]	[illegible]
-9	49	44
-10	54	52
H K=	-6 L=	3
0	67	65
-1	142	-131
1	68	67
2	68	-66
3	44	-40
-3	90	95
4	41	37
-4	89	92
5	162	161
-5	44	50
-7	168	168
-8	41	36
-9	68	68
9	126	132
10	55	-61
-11	111	111
H K=	-5 L=	3
0	136	120
-1	41	-43
2	74	-75
-2	113	-120
-3	110	-109
3	78	71
4	68	63
-4	142	147
-5	51	-49
-6	111	111
6	67	68
7	53	48
-7	107	-107
-8	153	150
8	147	149
-10	62	62
10	65	69
-12	60	61
H K=	-4 L=	3
1	132	138
-1	61	-53
-2	141	-136
2	56	49
-3	234	235
3	82	-78
4	204	197
5	217	212
-5	120	118
6	89	91
-7	248	245
7	72	73
-8	40	42
8	139	141
9	150	152
-9	78	75
-11	63	63
11	54	58
H K=	-3 L=	3
-2	127	114
-4	337	331
4	359	349
-5	178	173
5	47	-50
-6	98	91
6	114	114
-7	77	71
-8	246	236
8	230	234
-9	43	48
-10	46	48
10	88	89
-11	44	-48
12	71	79
-12	76	79
H K=	-2 L=	3
0	103	95
-1	158	-154
-2	135	139
2	267	-259
-3	130	133
-4	187	181
4	55	-50
-5	73	61
5	217	216
-6	80	73
6	156	-152
7	167	166
-7	188	176
8	66	-72
-8	47	48
9	209	210
-9	83	82
-11	109	110
11	55	63
H K=	-1 L=	3
0	317	311
-2	110	-107
2	138	-134
-3	74	-71
3	[illegible]	[illegible]
7	[illegible]	[illegible]
-7	34	32
9	121	-117
-9	85	85
-11	50	50
11	46	47
-13	65	64
H K=	3 L=	3
0	276	291
-1	103	103
1	141	-141
2	54	-59
-3	53	-52
3	34	-30
-4	284	289
4	225	234
5	160	-166
-5	82	81
-7	113	-115
7	49	-52
8	174	172
-8	135	134
9	38	-37
11	54	49
12	106	108
H K=	4 L=	3
-1	403	436
1	267	278
2	104	104
-2	62	-60
-3	290	282
3	336	330
4	64	-58
-4	45	-42
-5	206	197
5	51	54
6	61	65
7	135	134
8	39	37
-8	74	-74
9	50	41
-10	41	40
10	57	59
-11	43	-43
11	78	74
H K=	5 L=	3
0	445	464
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H K=	6 L=	3
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H K=	8 L=	3
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H K=	9 L=	3
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H K=	-9 L=	4
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H K=	-8 L=	4
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7	64	-68
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H K=	9 L=	7
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Table 1 (*a*) (*cont.*)

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H K= 13 L= 0   5 155 161   -2 232 225    5  52  53    9 171 172    3  70 -64    0 141 143    4 297 284    5  76 -76   -7  52  55   -1 133 131    8  69 -66   -6  96 -98   -4  61  61    2 115 113
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  6  56 -60    3 255 271   -3 145 151   -4  43  41   -9  80  79   -2  35  36   -3  10 -106   4 267 268    2  80   7   -4  76  74   -1  95  94   10  47  46   -1 160 157   -1  48  42    3  49  54
 -7  83  81   -3  52  50    4  73  65    5  55 -55  -10  42 -37   -3 139 133    3  97  93    5 127 126   -2 114 112    5  44  47    1 132 -134  11  49  55    2  59   9  H K= 10 L= 10  -3  47 -47
  9  97 103   -4  63 -64   -5 117 109  H K= 11 L= 2  11  61  64    3 136 -149  -4  93 -91   -5  50  48   -3 197 -194  H K=  5 L= 6   -2  99 103  H K=  1 L= 8   -2  47 -43    0  68  61  H K=  4 L= 13
H K= -9 L= 1   4 197 196    5 357 345   -1  68  65  -11  54 -53   -4  60  65   -5  74  73    6  38  38    3 120 115    0  44 -41    2  51  88   -1 278 291    3 128 126    2  45  42    1  43  38
  0  55  58   -5 287 281   -6  59  51    3  59  59  -12  76  79   -5  72  73    7 126 128   -6  86  85    4 143 142   -1 165 161    3  89 -86    1 265 270   -3 112 112  H K= -7 L= 11  H K= -2 L= 14
 -2 112 113    5 132 129   -7 200 194   -4  54 -50   12  74  74    5 141 140   -7  66  70   -7 130 -125  -4 154 156    1  92  95    4  10 107   -2  40 -38   -4  74 -75   -3  54 -61    2  66  65
  4  42  42   -6  52  50    7  57  56   -5  60  64  H K=  2 L= 3   6 140 -144  -8  82 -81    7 216 214   -5  84 -81   -2  72  41   -4 117 117   -3 268 275    4  60  62    5  48  45  H K= -1 L= 14
 -4  61  64    6 159 161   -8  74  72  H K= 12 L= 2   0  76 -77   -6  50 -47    8  51 -42    8 114 112    6  40  39   -3 111 114    5 244 -241   3 219 217   -5  77  77  H K= -6 L= 11   3  52  55
 10  70  74   -7  94  91    9  75  80    0  53  53    1 219 211   -7 153 144   -9 132 134   -8 148 146   -6  84  81    3  96  91   -5 178 173    4  39  43    5  61  57    1  89  87  H K=  2 L= 14
 12  46  48    7 212 210   -9  82  81    1  49  49   -1 290 281    7  97 100  -11  53  46   -9  57  95   -7  99 -98   -5  91  90   -7  56 -56   -5  83  82    6  62  58   -1  93  94   -2  53  43
H K= -8 L= 1  -8  61  69  -11 136 138    2  64  64    2 275 -280   9 181 187  H K=  8 L= 4  -12  57  62    7  98  99  H K= 10 L= 6   8  90  93    5  67  64   -7  67  67   -2  89 -89
  0  44  40    8  69  67  H K= -2 L= 2  -2  68  69   -2 277 277  -10  85 -83    1  51  54   12  58  60   -8  84  84    0  98  97    9  67 -65   -6  39 -40   -9  51  55    3  75  80
 -1 159 155   -9 130 135    0 109 140   -4  46  46    3 189 187   10  45 -43   -3  70 -70  H K=  2 L= 5   8  74  74    2  75  74   11  51  48    7  41  41  H K=  3 L= 9   -3  52  51
  1 332 334    9  64  63    3  52  44  H K= 13 L= 2  -3  89  79   11  77  83    3  80  75    1 183 180   12  48  54   -2  86  83  H K=  4 L= 7   8  54  57   -1  66  65    4  92  93
 -3 244 245   11 102 102   -3 134 -129  -1  65  64    4 186 -187 -11  60  66   -4  79  81   -1 200 207  H K= -3 L= 6  -4  55  57   -1 182 182    9  48  50    1  89 -88   -5  66  69
  3 136 133  -13  49  53    4 154 147  H K=-12 L= 3  -4  44  42  H K= -4 L= 4   4  73  79    2  76  75    0  59  55  H K= 11 L= 6   1 145 147  H K=  2 L= 8   3  98  98  H K= -5 L= 11
 -4  80  81  H K=  5 L= 1  -4 187 174   -1  76  78   -5 133 128    0 333 324    5  58  57   -2  39 -45   -1 199 199   -1  49  44    2  61  57    0 310 325   -3  83 -88    2  52  56
  5 195 193    0 234 230    5  58 -78    1 117 119    5 106 107   -1  53  53   -6  84  81   -3 144 142    1 345 342    3  43  37   -3 125 127   -1  67  69    4  72  70    4  55  55
 -5  49  47   -1  68  66   -6  73  74   -3  73  74   -6 123 121    1  69 -62    6  80  78    3 205 204   -2 173 -171  H K=-11 L= 7   3 128 132    1  81 -83   -6  74  75    6  55  51
 -7  73  76    1  99 -102   6  77  77    3  67  64    6 219 -213  -2 175 173   -7  66 -68    4  71 -69   -3 163 168    0  71  74    4  78 -77   -2 227 230    6  47  47  H K= -4 L= 11
```

Table 1 (*b*). *Unobserved reflections with calculated value greater than $F_{\rm min}$*

First column is h followed by k and $F({\rm calc}) = 3{\cdot}3F({\rm calc})$ absolute $F_{\rm min} = 66$. Number of reflections less than $F_{\rm min} = 1479$ Unobserved reflections were not included in the refinement.

```
                FMIN < |F(CALC)| < 2.0×FMIN            (15)

 L =  0    8 -9  57    L =  2   12 -1  47    L =  6    L = 10
 0  5  57  -1 -3  68  -8 -7  45   1. =  4   2 -9  45  -1  0  49
-7  7  55  10  0  48   9 -4  47   7 -4  68    L =  8
 L =  1   -4  8  46  10 -1  48   8  3  46   5  9  46

           2.0×FMIN < |F(CALC)| < 3.0 × FMIN           (10)

 L =  1     L =  2   -2  0 107   1-11 109    L =  7    2  5 129
-2 -1 101  -1 -4  90  0  0 122    L =  5   -5 -2 117
-2  0 131  -1 -3 116   L =  4    6  0 111    L =  8

                 3.0 × FMIN < |F(CALC)|                (41)

 L =  0   -3 -4 485  -4  0 227   L =  2   -3 -1 246  -1  0 208   1  1 448
 2  0 509  3 -4 299  -1  0 454   1 -5 314 -1 -1 282   1  0 202   0  2 397
-1  1 468  2 -3 324   1  0 480   1 -3 508  0  2 219   2  0 142   0  4 450
 1  1 513 -1 -2 302   2  0 159  -2 -2 426   L =  3   0  1 697    L =  5
-1  3 279  1 -2 595  -2  1 165  -1 -2 138 -1 -3 248    L =  4   -3  1 260
 0  4 656  2 -2 218   0  1 509   1 -2 165  0 -3 197   0  0 758
 L =  1    0 -1 481   1  2 327   2 -2 375  1 -3 184  -1  1 435
```

precipitated immediately and was filtered. This product was recrystallized by making an ethanol suspension and adding water drop-wise until the solid dissolved. Greenish-yellow, air-sensitive crystals separated from the solution in the course of 24–48 hours. These were dried *in vacuo* yielding single crystals suitable for X-ray diffraction. A needle crystal $0{\cdot}36 \times 0{\cdot}43 \times 0{\cdot}60$ mm was mounted with the long direction as the rotation axis (c). Preliminary Weissenberg and precession photographs ($hk0 \ldots hk7$, $h0l \ldots h2l$, $0kl \ldots 2kl$) indicated a triclinic cell (*International Tables for X-ray Crystallography*, 1965), with $a = 14{\cdot}1$ (1), $b = 23{\cdot}5$ (2), $c = 16{\cdot}4$ (1) Å, $\alpha = 89{\cdot}2$ (1), $\beta = 87{\cdot}9$ (1), $\gamma = 90{\cdot}9$ (1)°, and $Z = 12$. The systematic extinction for general hkl reflections with the crystal in this orientation was: $h + k = 2n + 1$ which demands a C-centered cell.

The crystal was aligned on an automated Picker full-circle diffractometer by variations of well known methods (Busing & Levy, 1967). Lattice constants were determined by least-squares refinement (Spofford, 1967) of the setting angles of 14 reflections that had been carefully centered on this apparatus. Using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71068$ Å) the lattice constants at room temperature are: $a = 14{\cdot}130 \pm 0{\cdot}009$, $b = 23{\cdot}601 \pm 0{\cdot}013$, $c = 16{\cdot}436 \pm 0{\cdot}010$ Å, $\alpha = 89{\cdot}9 \pm 0{\cdot}02$, $\beta = 87{\cdot}9 \pm 0{\cdot}1$, $\gamma = 90{\cdot}8 \pm 0{\cdot}1°$. This centered cell was subsequently reduced to a primitive cell with lattice constants $a = 9{\cdot}660 \pm 0{\cdot}005$, $b = 9{\cdot}581 \pm 0{\cdot}006$, $c = 9{\cdot}880 \pm 0{\cdot}007$ Å, $\alpha = 90{\cdot}8 \pm 0{\cdot}1$, $\beta = 87{\cdot}4 \pm 0{\cdot}1$, $\gamma = 92{\cdot}0 \pm 0{\cdot}1°$ by the following transformations: $h_p = (3h_c - k_c - 2l_c)/6$; $k_p = (k_c - l_c)/3$; $l_p = (3h_c - k_c - l_c)/6$. The atomic parameters *etc.* are based upon this cell. The reduced cell is $a = 13{\cdot}501$ (5), $b = 9{\cdot}581$ (6), $c = 9{\cdot}880$ (7) Å, $\alpha = 90{\cdot}8$ (1) $\beta = 134{\cdot}4$ (1), $\gamma = 90{\cdot}8$ (1)°.

The intensities of 3789 independent reflections were recorded by the θ–2θ scan technique using unfiltered Mo $K\alpha$ radiation at room temperature. All independent reflections to $2\theta = 60°$ were measured.* The peaks were scanned for 45 sec (1·5° 2θ) and backgrounds were estimated by stationary counting for 20 sec at $\pm 0{\cdot}75°$ (2θ) of the peak maximum. Integrated intensities were calculated assuming a linear variation in background from the function: $I_{\text{net}} = I_{\text{scan}} - 1{\cdot}125\,(B_1 + B_2)$ where B_1 and B_2 are the background counts. Low angle reflections were scanned at a narrower width to prevent problems from the β peak and were then scaled accordingly. A reflection was considered nonzero if I_{net} was greater than $3{\cdot}5 \times 1{\cdot}125\,(B_1 + B_2)^{1/2}$. 3005 reflections were found to meet this criterion. A standard reflection (one of average intensity) was measured after every ten reflections to monitor the stability of operation during the data collection. Deviation of the standard peak from the average during the entire data collection was less than 1·5 standard deviations with slightly less peak-to-peak variation. The take-off angle and crystal-to-counter, and counter-to-source distances were 3·7° and 18 and 23 cm respectively; and the receiving aperture at the counter was 6 mm wide by 8 mm high. The peak width at half-peak height for an average reflection was 0·31° (in 2θ) at the 3·7° take-off angle, indicating a reasonable mosaic spread for the peaks. The counting rate never exceeded 5000 counts per second and no attenuators were used. 575 symmetry-related reflections were measured and found to be in excellent agreement; apart from these only independent reflections were scanned. The linear absorption coefficient (μ) for this compound with Mo $K\alpha$ radiation is 17·6 cm^{-1}. No corrections for absorption* were made, but anomalous dispersion corrections were included in the refinement. Lorentz–polarization corrections were made, and the intensities reduced to structure factors.

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* A number of reflections were carefully examined, and it was found that with a suitably narrow choice of scan width the Mo $K\beta$ peak could be avoided. This procedure gave a better background estimate for all but a few low order or axial reflections than with the usual Zr filter. For those reflections where the Mo $K\beta$ reflections clearly created problems, the reflections were measured with a filter and scaling was accomplished *via* the standard reflection that was also measured with the Zr filter. In general, the reflections for which Mo $K\beta$ created problems could be identified by examination of the backgrounds of each peak.

Table 2. *Final atomic positional and thermal parameters and estimated standard deviations*

E.s.d. of last figure in parentheses.

Anisotropic temperature factors of the form:

$$\exp -[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl] \times 10^4$$

	x	*y*	*z*		*x*	*y*	*z*
Ni(1)	0·0000 (–)	0·0000 (–)	0·0000 (–)	C(3)	0·5720 (4)	0·3482 (4)	0·1717 (4)
Ni(2)	0·5000 (–)	0·5000 (–)	0·5000 (–)	C(7)	0·5391 (6)	0·2949 (6)	0·0327 (5)
S(1)	−0·0202 (1)	−0·2511 (1)	0·0487 (1)	N(3)	0·6953 (4)	0·3223 (5)	0·2141 (4)
S(2)	−0·0661 (1)	0·0512 (1)	0·2383 (1)	C(4)	0·4499 (4)	0·1748 (4)	0·6701 (4)
S(3)	0·4538 (1)	0·4370 (1)	0·2639 (1)	C(8)	0·4853 (5)	0·0318 (5)	0·7151 (5)
S(4)	0·5538 (1)	0·2575 (1)	0·5529 (1)	N(4)	0·3408 (4)	0·2294 (4)	0·7291 (4)
Cl(1)	−0·2487 (1)	−0·0266 (1)	−0·0219 (1)	H(1)	0·207 (5)	−0·130 (6)	0·191 (5)
Cl(2)	0·2499 (1)	0·4719 (1)	0·5332 (1)	H(2)	0·219 (7)	−0·256 (7)	0·290 (7)
C(1)	0·0834 (4)	−0·3089 (5)	0·1667 (4)	H(3)	0·194 (5)	0·175 (6)	0·203 (6)
C(5)	0·0653 (6)	−0·4557 (5)	0·2163 (5)	H(4)	0·202 (5)	0·260 (6)	0·348 (6)
N(1)	0·1800 (4)	−0·2300 (5)	0·2194 (4)	H(5)	0·762 (8)	0·296 (9)	0·151 (9)
C(2)	0·0353 (4)	0·1557 (4)	0·3315 (4)	H(6)	0·730 (5)	0·370 (5)	0·295 (6)
C(6)	−0·0176 (5)	0·2033 (6)	0·4693 (5)	H(7)	0·285 (6)	0·175 (7)	0·802 (6)
N(2)	0·1588 (4)	0·2025 (4)	0·2907 (4)	H(8)	0·313 (5)	0·319 (6)	0·704 (5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}		*B*
Ni(1)	57 (1)	69 (1)	62 (1)	5 (1)	−7 (1)	4 (1)	H(1)	4 (3)
Ni(2)	52 (1)	74 (1)	58 (1)	4 (1)	−3 (1)	6 (1)	H(2)	6 (5)
S(1)	106 (1)	69 (1)	85 (1)	4 (1)	−38 (1)	7 (1)	H(3)	5 (5)
S(2)	73 (1)	94 (1)	64 (1)	−6 (1)	0 (1)	−7 (1)	H(4)	4 (3)
S(3)	68 (1)	103 (1)	60 (1)	16 (1)	−7 (1)	−7 (1)	H(5)	8 (6)
S(4)	85 (1)	77 (1)	73 (1)	11 (1)	11 (1)	15 (1)	H(6)	3 (2)
Cl(1)	60 (1)	105 (1)	81 (1)	2 (1)	−7 (1)	13 (1)	H(7)	6 (3)
Cl(2)	56 (1)	108 (1)	82 (1)	0 (1)	−1 (1)	6 (1)	H(8)	3 (2)
C(1)	82 (5)	89 (5)	59 (4)	27 (4)	1 (3)	7 (3)		
C(5)	151 (7)	82 (6)	115 (6)	14 (5)	−22 (5)	28 (5)		
N(1)	96 (5)	135 (6)	84 (4)	11 (4)	−30 (3)	23 (4)		
C(2)	89 (5)	68 (4)	64 (4)	12 (4)	−11 (3)	3 (3)		
C(6)	138 (7)	120 (7)	78 (5)	5 (5)	−3 (4)	−18 (4)		
N(2)	104 (5)	114 (5)	100 (5)	−22 (4)	−13 (4)	−20 (4)		
C(3)	96 (5)	65 (5)	73 (4)	6 (4)	3 (3)	8 (3)		
C(7)	159 (7)	124 (7)	70 (5)	11 (6)	−4 (5)	−20 (4)		
N(3)	104 (5)	161 (7)	116 (5)	55 (5)	−6 (4)	−27 (5)		
C(4)	83 (5)	75 (5)	73 (4)	−12 (4)	−14 (3)	12 (3)		
C(8)	140 (7)	79 (5)	110 (6)	8 (5)	−9 (5)	26 (4)		
N(4)	95 (5)	112 (5)	127 (5)	2 (4)	30 (4)	44 (5)		

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* The neglect of the absorption correction no doubt makes our assessment of error optimistic. At the time of the solution of this structure (three years ago) our absorption program was not operating satisfactorily, Afterwards, we did not feel that the structure warranted the correction and subsequent computing time needed to refine the structure again. We now make routine absorption corrections on all data.

Structure determination

Assuming space group $P\bar{1}$ the structure was solved by standard heavy-atom methods (Harris, 1964) and refined by the full-matrix isotropic least-squares method (Busing, Martin & Levy, 1962) without hydrogen atom contributions to an R of 0·089. Anisotropic refinement of all nonhydrogen parameters converged to an R of 0·048. A difference map at this point located all the amide hydrogen atoms, but the methyl hydrogen atoms could not be located.

A full-matrix least-squares refinement of all parameters using isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for all other atoms resulted in $R=0{\cdot}034$, $wR=0{\cdot}039$, and standard error of an observation of unit weight = 0·500.*

The function minimized in the least-squares refinement was $\sum w(|F_o|-|F_c|)^2$ where F_o and F_c are the observed and calculated structure factors with unit weights. Scattering factors for Ni^{2+}, Cl^-, and neutral sulfur, carbon and nitrogen were from Cromer & Waber (1965). Hydrogen atom scattering factors were from Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections were included in the structure factor calculations by addition to F_c (Ibers & Hamilton, 1964); the values for $\Delta f'$ and $\Delta f''$ for nickel, chlorine and sulfur were those given by Cromer (1965). The final tabulation of observed and calculated structure factors is in Table 1 (*a*). Unobserved data were not used in the structure refinement but selected reflections are included in Table 1(*b*). Final atomic positional and thermal parameters are listed in Table 2. Interatomic distances and angles, root-mean-square components of thermal displacement, dihedral angles between normals to planes, and their errors were computed (Busing, Martin & Levy, 1964) with the parameter and variance-covariance matrix from the last cycle of least-squares refinement and are listed in Tables 3, 4 and 5. Appropriate least-squares planes (Spofford, 1966) are also listed in Table 5.

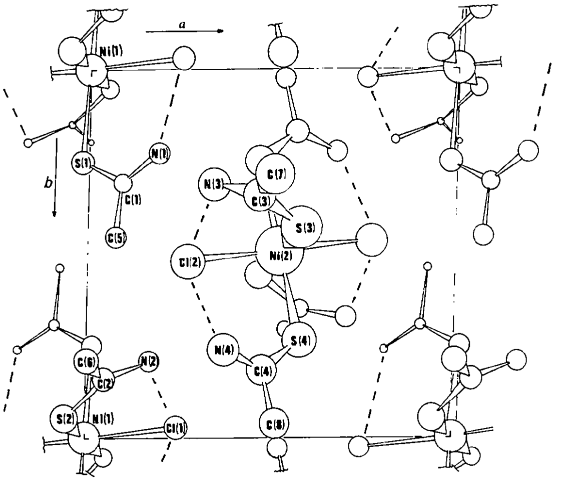

Fig. 1. Molecular packing diagram of the contents of the unit cell of *trans* dichlorobis(thiacetamide)Ni(II) looking down the $[00\bar{1}]$ direction.

Table 3. *Interatomic and intermolecular distances and bond angles*

Interatomic distances and angles

Bonding distances (Å)		Angles (°)	
Ni(1)–S(1)	2·460 (1)	S(1)—Ni(1)–S(2)	89·38 (4)
Ni(1)–S(2)	2·458 (1)	S(1)—Ni(1)–Cl(1)	83·05 (4)
Ni(2)–S(3)	2·459 (1)	S(2)—Ni(1)–Cl(1)	83·34 (3)
Ni(2)–S(4)	2·466 (1)	S(3)—Ni(2)–S(4)	91·97 (4)
Ni(1)–Cl(1)	2·427 (1)	S(3)—Ni(2)–Cl(2)	96·43 (4)
Ni(2)–Cl(2)	2·430 (1)	S(4)—Ni(2)–Cl(2)	96·55 (4)
S(1)—C(1)	1·682 (4)	Ni(1)–S(1)—C(1)	116·2 (2)
S(2)—C(2)	1·674 (4)	Ni(1)–S(2)—C(2)	120·3 (1)
S(3)—C(3)	1·676 (4)	Ni(2)–S(3)—C(3)	119·1 (2)
S(4)—C(4)	1·686 (4)	Ni(2)–S(4)—C(4)	117·3 (2)
C(1)--C(5)	1·497 (6)	S(1)--C(1)--C(5)	120·0 (3)
C(2)--C(6)	1·503 (6)	S(1)—C(1)—N(1)	122·5 (3)
C(3)—C(7)	1·502 (6)	C(5)—C(1)—N(1)	117·5 (4)
C(4)--C(8)	1·502 (6)	S(2)—C(2)—C(6)	119·2 (3)
C(1)--N(1)	1·304 (6)	S(2)—C(2)—N(2)	124·0 (3)
C(2)—N(2)	1·308 (6)	C(6)—C(2)—N(2)	116·8 (4)
C(3)—N(3)	1·313 (6)	S(3)—C(3)—C(7)	119·8 (3)
C(4)—N(4)	1·303 (6)	S(3)—C(3)—N(3)	123·3 (3)
Avg. N–H*	0·89 (6)	C(7)—C(3)—N(3)	116·9 (4)
		S(4)—C(4)—C(8)	119·4 (3)
		S(4)—C(4)—N(4)	123·9 (3)
		C(8)—C(4)—N(4)	116·7 (4)
		Avg. C–N–H†	118 (4)
		Avg. H–N–H‡	122 (5)

* Range of N–H distances: 0·81–1·15 Å with e.s.d.'s of 0·05–0·08 Å.

† Range of C–N–H angles: 114–121° with e.s.d.'s of 3–5°.

‡ Range of H–N–H angles: 113–128° with e.s.d.'s of 4–5°.

Intramolecular H-bonded distances (Å)

Ni(1)		Ni(2)	
H(1)–Cl(1)	2·06 (6)	H(8)–Cl(2)	2·40 (6)
N(1)–Cl(1)	3·192 (4)	N(4)–Cl(2)	3·214 (4)
H(1)–N(1)	1·15 (6)	N(4)–H(8)	0·89 (6)
H(3)–Cl(1)	2·33 (6)	H(6)–Cl(2)	2·26 (6)
N(2)–Cl(1)	3·228 (4)	N(3)–Cl(2)	3·213 (4)
N(2)–H(3)	0·94 (6)	H(6)–N(3)	0·99 (6)

Table 3 (*cont.*)

Shortest possible intermolecular H-bonded distances (Å)

Cl(2)–H(4)	2·80 (6)	Cl(2)–N(2)	3·611 (4)	N(2)–H(4)	0·84 (6)
Cl(1)–H(7)	2·58 (8)	Cl(1)–N(4)	3·568 (4)	N(4)–H(7)	1·06 (6)

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* $R=(\sum||F_o|-|F_c||)/\sum|F_o|$. Weighted $R=\{[\sum w(F_o-F_c)^2]/\sum wF_o^2\}^{1/2}$. Standard error $=\frac{[\sum w(F_o-F_c)^2]^{1/2}}{(NO-NV)}$ where NO = 2953 observations: NV = 173 variables.

Table 4. *R.m.s. component of thermal displacement along principal axes* (Å) (*e.s.d. in parentheses*)

	1	2	3
Ni(1)	0·159 (1)	0·176 (1)	0·181 (1)
Ni(2)	0·156 (1)	0·166 (1)	0·188 (1)
S(1)	0·165 (1)	0·183 (2)	0·249 (1)
S(2)	0·174 (1)	0·182 (1)	0·216 (1)
S(3)	0·168 (1)	0·174 (1)	0·225 (1)
S(4)	0·170 (1)	0·184 (1)	0·222 (1)
Cl(1)	0·167 (1)	0·193 (1)	0·227 (1)
Cl(2)	0·163 (1)	0·200 (1)	0·226 (1)
C(1)	0·167 (6)	0·171 (5)	0·227 (6)
C(5)	0·171 (7)	0·248 (6)	0·272 (6)
N(1)	0·164 (5)	0·232 (5)	0·259 (5)
C(2)	0·166 (6)	0·180 (6)	0·210 (5)
C(6)	0·186 (6)	0·244 (7)	0·255 (6)
N(2)	0·181 (5)	0·230 (5)	0·257 (5)
C(3)	0·169 (6)	0·190 (6)	0·217 (6)
C(7)	0·176 (6)	0·247 (7)	0·274 (7)
N(3)	0·182 (6)	0·235 (5)	0·303 (6)
C(4)	0·172 (6)	0·179 (5)	0·220 (5)
C(8)	0·173 (7)	0·245 (6)	0·257 (6)
N(4)	0·170 (4)	0·220 (5)	0·288 (6)

Table 5. *Least-square planes of the type* $Ax+By+Cz-D=0$

x, y and z refer to an internal orthogonal coordinate system (*International Tables for X-ray Crystallography*, 1967).

Plane No.	1	2	3	4
A	0·6308	−0·4422	0·3177	−0·5760
B	−0·2920	0·8020	0·8611	−0·3912
C	−0·7189	−0·4017	−0·3969	−0·7178
D	−0·3022	0·3348	−3·9282	8·0288

Atom/plane No.	1	2	3	4
S(*I*)*	−0·001 (1)	0·003 (1)	0·001 (1)	−0·004 (1)
C(*I*)	0·004 (4)	−0·009 (4)	−0·002 (4)	0·012 (4)
C(*I*+4)	−0·001 (5)	0·003 (5)	0·001 (5)	−0·004 (5)
N(*I*)	−0·001 (4)	0·004 (4)	0·001 (5)	−0·005 (4)

* *I* refers to plane number. Hydrogen atoms were all within 3 e.s.d.'s (0·07 Å) of their particular thioacetamide plane.

Dihedral angles between normals of planes

Plane 1	Plane 2	Angle
Ni(1)–S(1)–S(2)	Ni(1)–S(1)–C(1)	59·3 (2)°
Ni(1)–S(1)–S(2)	Ni(1)–S(2)–C(2)	54·6 (2)
Ni(2)–S(3)–S(4)	Ni(2)–S(3)–C(3)	51·4 (2)
Ni(2)–S(3)–S(4)	Ni(2)–S(4)–C(4)	62·9 (2)
Ni(1)–S(1)–C(1)	S(1)—C(1)–N(1)	7·4 (4)
Ni(1)–S(2)–C(2)	S(2)—C(2)–N(2)	7·8 (4)
Ni(2)–S(3)–C(3)	S(3)—C(3)–N(3)	7·2 (5)
Ni(2)–S(4)–C(4)	S(4)—C(4)–N(4)	3·1 (5)

Description and discussion of structure

The structure may be described as isolated molecular units, Ni(tac)$_4$Cl$_2$ interacting with one another only by weak hydrogen bonds and/or van der Waals forces (Fig. 1). Each nickel atom has a coordination number of six with four sulfur atoms in a plane and two chlorine atoms in *trans* apical positions. Since the nickel atoms lie on crystallographic centers of symmetry (Fig. 2), the two nickel–chlorine distances for each metal atom must be identical. This is in marked contrast to *trans*-Nitu$_4$Cl$_2$, in spite of similarities in the spectra of these two compounds. In terms of the immediate coordination number and geometry about the Ni atom the present structure is more akin to *trans*-dichlorotetrakis(trimethylenethiourea)Ni(II), (TMeT)$_4$NiCl$_2$, and the dimorphic forms of *trans*-dichlorotetrakis(ethylenethiourea)Ni(II) (ETU)$_4$NiCl$_2$. In the present case the two crystallographically independent Ni–Cl distances are within 0·003 Å of one another and are not significantly different from the shorter Ni–Cl distance found in *trans* Nitu$_4$Cl$_2$ nor from the Ni–Cl distances found in *trans* (TMeT)$_4$NiCl$_2$ and *trans* (ETU)$_4$NiCl$_2$.

The thioacetamide groups are all oriented such that the methyl groups are turned to the outside. This orientation comes about due to fairly substantial N–H···Cl intramolecular hydrogen bonding, see Fig. 2(*a*) and (*b*) and Table 3. The shortest N···Cl intermolecular distances are at least 0·3 Å longer; consequently, the intermolecular hydrogen bonding is less important than the intramolecular hydrogen bonding. The thioacetamide groups remain planar upon binding with the metal, but these planes are tilted (52–64°) and twisted (3–7°). The tilt is defined as the dihedral angle between the NiS$_4$ plane and the Ni–S–C plane, whereas the twist is defined as the dihedral angle between the Ni–S–C plane and the thioacetamide plane (Table 5). The twist values found in the present structure analysis are comparable to the small (~2°) values found in Nitac$_4$Br$_2$ (Spofford & Amma, 1971) but are much less than the 17–28° usually found in thiourea complexes. (Nitac$_4$Br is a square planar NiS$_4$ unit with only nonbonded Ni–Br distances.) The four independent Ni–S distances are 2·460 (1), 2·458 (1), 2·459 (1) and 2·466 (1) Å. These Ni–S distances are in good agreement with those found in Nitu$_4$Cl$_2$, Ni(TMeT)$_4$Cl$_2$, Ni(ETU)$_4$Cl$_2$ and Nitu$_2$(SCN)$_2$ (Capacchi, Gasparri, Nardelli & Pelizzi, 1968) but are approximately 0·2 Å longer than those found in the four-coordinate Nitac$_4$Br$_2$ (Spofford, Boldrini & Amma, 1970). This difference between 'octahedral' nickel(II) and 'square planar' nickel(II) metal-ligand distances is to be expected.

The carbon–sulfur distance average of 1·679 Å with individual errors of ±0·004 Å seems to be significantly shorter than the 1·713 (6) Å found for the free thioacetamide ligand (Truter, 1960) but more than likely it results from an optimistic assessment of error in the present structure analysis as well as that in thioacetamide.

The carbon–nitrogen and carbon–carbon distances lie within one standard deviation of the average of 1·307 Å with individual errors of ±0·006 Å, and 1·502 Å with individual errors of ±0·006 Å respectively. Both of these values are expected for this ligand. The angles within the thioacetamide ligand are also those expected. The Ni–S–C angles of 116–120° in the present structure are somewhat larger than the 107–115° found in thiourea complexes as well as those found in Nitac$_4$Br$_2$ (110–114°). These differences are no doubt dependent upon differences in detail in hydrogen bonding rather than upon differences in bonding to sulfur. In fact, the differences in the tilt angles between the present structure and Nitac$_4$Br$_2$ can be correlated with hydrogen bonding. In Nitac$_4$Br$_2$, two independent tilt angles are 173 (2) and 175 (2)°, and in the present structure they are 52–64°. In the bromide, the bromines are in essentially axial positions with S–Ni–Br angles of 71–75° but with long Ni–Br distances of 3·599 (4) Å, yet all four of the Br–N hydrogen bonded distances are 3·30 Å. In the present structure the Ni–Cl distances are much shorter at 2·43 Å with smaller tilt angles of 52–64° and Cl–N hydrogen bonded distances of 3·2 Å. The corresponding distance in *trans* Nitu$_4$Cl$_2$ is 3·23 (3) Å.

This research was partially funded by National Institutes of Health Grant No. GM-13985.

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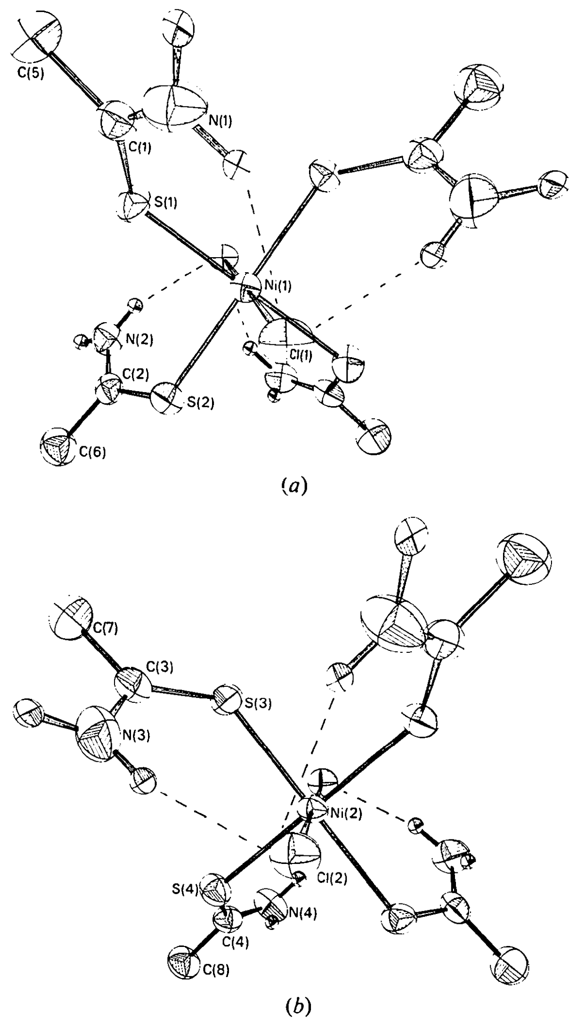

(*a*)

(*b*)

Fig. 2. (*a*) *ORTEP* drawing of *trans*-dichlorobis(thioacetamide) Ni(II) molecule containing Ni(1). (*b*) *ORTEP* drawing of *trans*-dichlorobis(thioacetamide)Ni(II) molecule containing Ni(2). Possibly significant hydrogen bonds are shown by dotted lines. We are grateful for the cooperation of Professor G. A. Jeffrey's research group at the University of Pittsburgh for these calculations.

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The Crystal Structure of *N*,*N*-Bis-2-chloroethyl-*N'*,*O*-propylene Phosphoric Ester Diamide Monohydrate (Endoxan)

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(*Received* 28 *February* 1972)

Crystals of endoxan were crystallized from an ether solution at −10 °C. The crystals are triclinic, with space group $P\bar{1}$ and cell dimensions: $a = 13{\cdot}402$, $b = 8{\cdot}669$, $c = 6{\cdot}003$ Å, $\alpha = 100{\cdot}3$, $\beta = 96{\cdot}4$ and $\gamma = 106{\cdot}8°$. The structure was solved by direct methods for phase determination, and successive Fourier syntheses. The structure was subsequently refined by the full-matrix least-squares method to an R value of 0·042 for 2255 reflexions collected on an automatic diffractometer with Mo $K\alpha$ radiation. All the hydrogen atoms were located in a difference Fourier synthesis. The molecules are held together in three dimensions by one N–H···O and two O–H···O hydrogen bonds.

Introduction

The study of the crystal structure of endoxan was carried out to collect new data for those interested in the use of citostatics for the chemotherapy of cancer tumours. Endoxan has partially solved some of the main problems caused by nitrogen mustard in the human organism (Arnold & Bourseaux, 1958). Mustards were used for a long time in the therapy of neoplastic diseases, since they can control the smaller metastases which are innaccessible by other techniques such as surgery and radiation.

The citostatic effect of the chloroalkyl-amine of the nitrogen mustard stems from the large lability of the chlorine atoms located in the β-position of the nitrogen atom. According to Ross (1945), the dissociation of these compounds results in a positively charged carbonium ion with biological activity. The amine groups of the mustard behave as alkylating agents in a biological medium reacting with active atoms of H. This is similar to the behaviour of SH groups in proteins or enzymes producing lessening of growth or even a destruction of the malignant cells.

Experimental

The crystals of endoxan were kindly supplied by ASTA-WERKE laboratories (Chemische fabrik, Westfalia, Germany). The samples were recrystallized from an ether solution prepared by means of ether extraction in a Soxhlet aparatus and subsequent cooling of the solution to a temperature of −10°. The crystals are prismatic with the longest dimension along the c axis. Preliminary cell dimensions were obtained from Weissenberg photographs taken from a crystal rotated about the b and a axes. Precise unit-cell constants were determined by the least-squares method from the angular settings of 24 independent reflexions measured on an AED Siemens diffractometer. The density was measured by flotation in a mixture of carbon tetrachloride and n-heptane.

Crystal data

$Cl_2PN_2O_2C_7H_{15}.H_2O$, M.W. 278·98, m.p. 40–41 °C, crystal size: 0·15 × 0·26 × 0·33 mm. Triclinic, $a = 13{\cdot}402$ (20), $b = 8{\cdot}669$ (10), $c = 6{\cdot}003$ (8) Å, $\alpha = 100{\cdot}3$ (5), $\beta = 96{\cdot}4$ (5), $\gamma = 106{\cdot}8$ (5)°, $D_m = 1{\cdot}41$ g.cm^{-3}, $D_x = 1{\cdot}423$ g.cm^{-3}, $Z = 2$. Linear absorption coefficient for Mo $K\alpha$ radiation $\mu = 4{\cdot}31$ cm^{-1}.

The statistical averages suggest that the electron density distribution within the unit cell is centrosymmetric. Hence the space group $P\bar{1}$ was assumed for the study, and this was confirmed by the successful structure analysis.

The reflexion intensities were measured on an automatic diffractometer (four circle AED Siemens) using Zr-filtered Mo $K\alpha$ radiation. Intensities for 2552 reflexions were measured by scanning in the θ–2θ mode