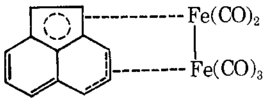
TABLE VI

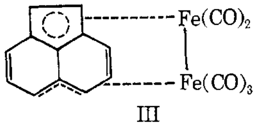
LEAST-SQUARES PLANES WITHIN THE $C_{12}H_8Fe_2(CO)_5$ MOLECULE[a-c]

Atom	Dist, Å	Atom	Dist, Å
(A) $0.6305X + 0.5050Y + 0.5892Z - 8.3025 = 0$			
C(1)*	−0.006 (9)	C(3)	−0.017
C(2)*	−0.003 (9)	C(8)	−0.011
C(9)*	+0.011 (8)	C(4)	−0.224
C(12)*	−0.015 (8)	C(7)	−0.215
C(11)*	+0.013 (8)	C(5)	−0.440
		C(6)	−0.411
Fe(1)	−1.725	C(10)	−0.158
(B) $0.8355X + 0.1618Y + 0.5250Z - 7.0556 = 0$			
C(5)*	0.000	Fe(2)	−1.837
C(10)*	0.000		
C(6)*	0.000		
(C) $-0.4446X - 0.3724Y + 0.8146Z + 1.2650 = 0$			
C(10)*	+0.001 (8)	C(5)	−1.268
C(12)*	−0.001 (8)	C(6)	+1.258
Fe(1)*	0.000 (1)	C(13)	−1.303
Fe(2)*	0.000 (1)	C(14)	+1.196
C(1)	+0.759	O(1)	−2.196
C(2)	−0.656	O(2)	+1.916
C(9)	−1.162	C(15)	−1.341
C(11)	+1.192	C(16)	+1.368
C(3)	−2.414	O(3)	−2.198
C(8)	+2.463	O(4)	+2.323
C(4)	−2.446	C(17)	+0.041
C(7)	+2.490	O(5)	+0.067

[a] All planes are expressed in Cartesian coordinates. The transformations to natural cell coordinates are $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$. [b] A plane is derived using unit weights for atoms marked with asterisks. [c] The angle between planes A and B is 23° 25′.



II



III

within the six-membered rings has been wholly disrupted. The stability of this compound is thus a considerable tribute to the combined strength of π-cyclopentadienyl→iron and π-allyl→iron bonding.

The preference for III over II furthermore demonstrates the importance of steric effects. In azulenediiron pentacarbonyl[2] (I) atoms of the seven-membered ring are bent out of the plane of the five-membered ring by as much as 0.91 Å, and the stereochemistry of the azulene ligand adapts to conform to electronic requirements. In the case of acenaphthylenediiron pentacarbonyl, the organic ligand is more rigid than azulene and the planar configuration III is more in keeping with iron–iron bond length requirements than is the planar configuration II. In this case, then, the electronic requirements are subservient to the steric requirements of the relatively rigid polycyclic acenaphthylene framework. There is some distortion of the ligand from planarity, but Figure 1 shows this to be relatively slight.

Acknowledgments.—This work has been generously supported by the National Science Foundation (Grant No. GP-8077) and the Advanced Research Projects Agency (Contract No. SD-88). J. W. acknowledges, with gratitude, the receipt of a graduate national fellowship for 1968–1970 from Harvard University.

CONTRIBUTION FROM THE
ISTITUTO CHIMICO DELL'UNIVERSITÀ DI NAPOLI, NAPLES, ITALY

The Solid-State Structure of π-Allyldi(thiourea)nickel(II) Chloride

BY A. SIRIGU

Received July 25, 1969

The crystal structure of π-allyldi(thiourea)nickel(II) chloride has been determined by single-crystal X-ray diffraction methods. The crystals are orthorhombic with space group Pbca and cell parameters $a = 25.24$ (8) Å, $b = 11.17$ (4) Å, $c = 8.63$ (3) Å, with $Z = 8$, $d_{\text{calcd}} = 1.57$ g cm^{-3}, and $d_{\text{obsd}} = 1.5$ g cm^{-3}. With Cu Kα radiation 1113 intensities were measured by standard Weissenberg equiinclination photographic methods. The structure was solved by routine heavy-atom methods and refined by block-diagonal least-squares methods with anisotropic temperature factors for Ni, Cl, and S to a final conventional R factor of 0.096. The structure is made up of molecular ions π-$C_3H_5Ni(SC(NH_2)_2)_2^+$ and chloride ions. The shortest Ni–Cl distance is 3.445 ± 0.004 Å. The coordination of the ligands around the nickel atom in the positive molecular ion may be considered as square planar. The S_1NiS_2 angle (110.9 ± 0.1) is however definitely larger than that expected for a normal square-planar coordination. The carbon–carbon distances of the allyl group are equal within errors. The dihedral angle between the plane containing the carbon atoms of the allyl group and that containing the Ni, S_1, and S_2 atoms is 118 ± 3°. The crystal structure appears to be largely determined by the formation of hydrogen bonds between the NH_2 groups of the thiourea ligands and the chloride ions.

Introduction

The influence of thiourea on the efficiency of π-allylnickel halides as catalysts for the synthesis of dienoic esters was observed and discussed by Chiusoli and Merzoni.[1] They postulated the formation of an intermediate π-allylnickel(II)–thiourea complex. The existence of this complex was confirmed by Guerrieri[2] by the preparation of a series of compounds of the general formula π-alNiLL′X in which al is allyl, methallyl, or crotyl, L and L′ are thiourea, diisopropyl-

---

(1) G. P. Chiusoli and S. Merzoni, *Chim. Ind.* (*Milan*), **43**, 259 (1961).

(2) F. Guerrieri *Chem. Commun.*, 983 (1968).

TABLE I

Atomic Coordinates and Thermal Parameters[a]

	x	y	z	B, Å^2
Ni	0.0806 (1)	0.0451 (2)	0.1463 (3)	
S(1)	0.1244 (2)	0.2076 (3)	0.0724 (5)	
S(2)	0.1063 (2)	−0.1131 (3)	0.0117 (5)	
Cl	0.1743 (2)	−0.0544 (3)	0.4066 (4)	
C(1)	0.0252 (7)	−0.0648 (16)	0.2498 (23)	6.2 (4)
C(2)	0.0356 (10)	0.0410 (23)	0.3318 (29)	9.5 (6)
C(3)	0.0304 (8)	0.1499 (19)	0.2720 (25)	7.5 (5)
C(4)	0.1281 (5)	−0.0858 (11)	−0.1726 (17)	3.7 (3)
C(5)	0.1888 (5)	0.1763 (12)	0.0238 (17)	3.9 (3)
N(1)	0.2131 (5)	0.0745 (11)	0.0698 (16)	4.9 (3)
N(2)	0.2172 (5)	0.2552 (13)	−0.0583 (17)	5.8 (3)
N(3)	0.1504 (5)	−0.1768 (11)	−0.2525 (15)	4.8 (3)
N(4)	0.1263 (5)	0.0228 (10)	−0.2389 (15)	4.5 (2)

Anisotropic Thermal Parameters[b]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	4.57 (10)	3.54 (9)	3.90 (15)	−0.04 (9)	0.29 (10)	−0.40 (9)
S(1)	4.93 (17)	2.86 (12)	4.88 (25)	0.22 (13)	0.57 (16)	−0.46 (13)
S(2)	7.83 (24)	2.78 (12)	3.26 (22)	0.00 (14)	0.69 (19)	0.19 (12)
Cl	4.86 (16)	3.62 (13)	3.09 (21)	−0.06 (13)	0.21 (14)	0.09 (12)

[a] Standard deviations are given in parentheses. [b] The temperature factor is of the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

thiourea, or ethylenethiourea whereas X may be Cl, Br, or I. A further study of this argument has been recently reported by Chiusoli and coworkers.[3] They proposed for carbonylation of allylic halides to give methyl dienoates a reaction mechanism involving the formation of a catalytic five-coordinated nickel complex containing thiourea.

The crystal structure and coordination geometry of π-allyldi(thiourea)nickel(II) chloride, π-$C_3H_5Ni(SC(NH_2)_2)_2Cl$, determined by the single-crystal X-ray diffraction method is reported here.

Experimental Section

Crystals suitable for X-ray work were prepared by Guerrieri. The cell parameters were obtained from Weissenberg photographs using Cu Kα (1.5418 Å) radiation and are a = 25.24 (8) Å, b = 11.17 (4) Å, c = 8.63 (3) Å, Z = 8, d_{calcd} = 1.57 g cm^{-3}, and d_{exptl} = 1.5 g cm^{-3}. (d_{exptl} is an approximate value due to the air-sensitive nature of the compound. The determination was made by flotation in a mixture of CCl_4 and $CHCl_3$.) The space group Pbca was uniquely inferred from the analysis of the systematic absence. Reflections were of the types 0*kl* with *k* odd, *h*0*l* with *l* odd, and *hk*0 with *h* odd. A prism-shaped crystal of dimensions 0.2 × 0.2 × 0.4 cm was mounted about the long direction (c) and used to collect 1113 independent *hkl* planes of intensity data by standard multiple-film equiinclination techniques, for *hk*0–*hk*5. Nickel-filtered copper radiation (λ 1.5418 Å) was used. The mounting of another crystal of the same dimensions gave 0*kl* data by the same technique which were then used to reduce the *hk*0 · · · *hk*5 data to a common scale. The intensities were determined visually using a strip of comparison spots prepared with timed exposure of the crystal mounted about the c axis. The linear absorption coefficient was calculated to be 46.0 cm^{-1}. A cylindrical absorption correction gave a maximum difference in transmission factors of 10% and no absorption correction was made to the intensity data.

Determination and Refinement of the Structure

The nickel, sulfur, and chlorine atoms were located from a three-dimensional Patterson map, and the other nonhydrogen atoms were found by standard Fourier techniques. No effort was made to locate hydrogen atoms. The structure was refined by block-diagonal least squares. The function minimized was $R_w = \Sigma_{hkl}w(\Delta F)^2/\Sigma_{hkl}|F_o|^2$. Atomic scattering factors given by Hanson, *et al.*,[4] were utilized. A constant value of 3.1 e$^-$ was subtracted from the scattering factor of the nickel atom to take into account the real part of anomalous diffraction.[5] The following weighting scheme was used: $w = 1/(A + BF_o + CF_o^2)$; $A = {}^1/_9$; $B = 1/(18.0F_o(\min))$; $C = 2/(18.0F_o(\min)F_o(\max))$, where $F_o(\min)$ and $F_o(\max)$ are, respectively, the minimum and the maximum values of the observed structure factors. With individual isotropic temperature factors the refinement converged to an R of 0.142. Four cycles of anisotropic refinement of the Ni, Cl, and S atoms reduced R to the final value of 0.096. A final difference Fourier synthesis shows maxima of no more than 1.2 e$^-$ Å^{-3} electron density.

The final atomic coordinates and thermal parameters are given in Table I. Additional information about the thermal motion of nickel, sulfur, and chlorine atoms is given in Table II. A comparison between observed and calculated structure factors is reported in Table III.

TABLE II

RMS THERMAL DISPLACEMENTS AND ORIENTATION WITH RESPECT TO THE CRYSTALLOGRAPHIC AXES

	Rms displacements, Å	Direction cosines with respect to		
		a	b	c
Ni	0.241	0.039	−0.006	0.026
	0.224	−0.009	−0.037	0.102
	0.209	−0.001	0.081	0.048
S(1)	0.256	0.028	−0.003	0.081
	0.242	−0.028	−0.011	0.081
	0.189	−0.003	0.089	0.013
S(2)	0.314	0.040	0.000	0.009
	0.203	−0.003	0.018	0.113
	0.187	0.001	0.088	−0.023
Cl	0.247	0.040	−0.002	0.007
	0.214	0.001	0.089	0.010
	0.197	−0.002	−0.008	0.115

Discussion of the Structure

The relevant molecular parameters are reported in Table IV. As far as the purely geometrical arrangement of the ligand (including the chlorine atom) is concerned, the coordination around the nickel atom could be described as square pyramidal (see Figure 1). The nickel–chlorine interatomic distance (3.445 (4) Å) is, however, far larger than any other usually found in complexes containing Ni–Cl bonds (2.38 Å in $NiCl_2 \cdot 6H_2O$;[6] 2.32 (1) Å, 2.39 (1) Å in the paramagnetic square-pyramidal dimeric dichloro(2,9-dimethyl-1,10-phenanthroline)nickel(II);[7] 2.40 (2) Å, 2.52 (2) Å in the octahedral dichlorotetrakis(thiourea)nickel;[8] 2.27 Å in paramagnetic tetrahedral dichlorobis(triphenylphos-

---

(3) G. P. Chiusoli, M. Dubini, M. Ferraris, F. Guerrieri, S. Merzoni, and G. Mondelli, *J. Chem. Soc., C*, 2889 (1968).

(4) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(5) C. H. Dauben and D. H. Templeton, *ibid.*, **8**, 841 (1955).

(6) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, Interscience, New York, N. Y., 1965, p 788.

(7) H. S. Preston and C. H. L. Kennard, *Chem. Commun.*, 819 (1968).

(8) A. Lopez-Castro and R. Truter, *J. Chem. Soc.*, 1309 (1963).

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H	K	F_o	F_c
L=0			
4	0	335	-314
6	0	79	-36
8	0	16	11
10	0	100	102
12	0	23	-18
14	0	20	-13
18	0	35	-32
24	0	30	30
2	1	66	-63
2	2	112	115
2	3	119	130
2	4	30	-19
2	5	125	-116
2	6	26	21
2	7	122	-118
2	8	12	9
2	9	20	-14
2	11	23	-17
2	12	26	-19
2	13	23	17
4	1	20	-11
4	2	43	-38
4	3	132	-132
4	5	145	-146
4	7	151	-136
4	8	79	25
4	9	38	-34
4	10	40	-34
4	11	20	17
4	12	68	68
4	13	28	27
6	1	110	-84
6	2	71	-69
6	3	99	111
6	4	24	-17
6	5	43	43
6	6	37	30
6	7	60	61
6	8	63	-33
6	9	21	-17
6	11	26	18
6	12	31	26
6	13	28	-27
6	14	6	16
8	1	94	80
8	2	136	-135
8	3	70	66
8	4	37	-32
8	5	154	164
8	7	102	98
8	8	61	53
8	10	81	83
8	11	40	-35
8	13	17	-15
10	1	73	-73
10	2	42	43
10	3	100	100
10	4	25	-25
10	5	15	-11
10	6	39	-38
10	8	15	14
10	9	27	22
10	12	19	-15
10	13	17	20
12	1	28	22
12	2	132	137
12	3	86	88
12	4	19	13
12	5	64	66
12	7	29	-31
12	8	39	-39
12	9	16	15
12	10	67	-67
12	11	14	10
12	12	12	-12
12	13	11	-10
14	1	65	53
14	3	63	-58
14	4	60	56
14	5	28	-24
14	9	26	-27
14	1	19	17
16	1	55	-48
16	2	33	-28
16	3	116	-106
16	4	26	21
16	5	78	-79
16	6	13	14
16	7	32	-30
16	8	22	-16
16	9	23	-22
16	10	24	24
18	1	32	-37
18	2	40	-36
18	3	36	39
18	4	26	-22
18	5	23	22
18	6	21	-21
18	8	23	23
18	10	19	15
20	2	40	-46
20	3	31	32
20	4	44	-48
20	6	16	20
20	7	26	20
20	8	40	39
20	9	13	12
20	10	17	14
22	1	40	44
22	2	13	12
22	4	13	12
22	3	17	20
24	2	23	26
24	3	24	22
24	4	32	32
24	5	20	18
24	6	11	-11
24	7	19	17
24	8	21	-20
26	1	19	-18
26	5	16	-14
26	6	11	15
28	1	12	-12
28	2	15	11
28	3	20	-20
28	5	21	-22
28	6	8	-7
28	7	11	-12
0	2	196	209
0	4	64	48
0	6	84	-76
0	8	108	-99
0	10	28	-26
0	12	59	-61
0	14	16	-13
L=1			
1	1	145	145
2	1	157	-135
3	1	25	-25
4	1	109	-120
5	1	227	-204
6	1	165	-171
7	1	102	-107
8	1	39	36
9	1	144	142
10	1	118	115
11	1	20	8
12	1	51	-45
13	1	26	20
14	1	89	-91
15	1	51	44
16	1	30	-28
17	1	51	-44
18	1	13	-11
20	1	25	19
22	1	44	40
25	1	19	22
0	2	140	-147
1	2	92	-96
2	2	46	-50
3	2	63	63
4	2	53	55
5	2	22	20
6	2	62	65
7	2	94	-100
8	2	9	-9
9	2	64	61
11	2	38	55
13	2	11	13
14	2	63	-56
15	2	14	-16
16	2	12	14
17	2	46	-44
18	2	38	38
19	2	20	-19
20	2	12	8
21	2	41	43
23	2	18	16
24	2	14	-15
25	2	12	-16
26	2	11	-15
1	3	61	-64
2	3	61	-59
3	3	122	122
4	3	19	-26
6	3	47	-51
7	3	89	-81
8	3	16	12
9	3	31	-28
10	3	113	115
12	3	16	26
13	3	93	93
14	3	67	-76
15	3	16	16
16	3	30	-30
17	3	52	-58
20	3	12	12
22	3	12	6
0	4	41	26
1	4	42	-39
2	4	60	-60
3	4	38	27
4	4	26	-16
5	4	44	-39
6	4	159	163
7	4	72	-73
8	4	59	59
9	4	107	110
10	4	48	-44
11	4	86	96
12	4	51	-56
13	4	54	-53
14	4	63	-62
15	4	42	-45
16	4	21	18
18	4	34	37
21	4	20	23
24	4	12	-15
26	4	11	-16
2	5	9	-11
3	5	19	-21
4	5	30	-27
5	5	11	14
6	5	19	19
7	5	37	37
8	5	21	22
9	5	39	-34
11	5	15	-16
14	5	17	19
15	5	36	39
17	5	21	19
18	5	16	-18
19	5	41	-41
21	5	10	-9
23	5	14	14
25	5	14	14
0	6	65	-70
1	6	159	-153
2	6	49	-47
3	6	133	-136
4	6	49	47
5	6	51	49
6	6	104	101
7	6	63	61
8	6	14	13
9	6	47	50
10	6	24	-21
11	6	19	-18
12	6	24	-25
13	6	36	-33
14	6	47	-49
15	6	21	22
17	6	15	-17
18	6	27	32
19	6	25	-30
21	6	23	28
23	6	17	18
24	6	16	-15
26	6	16	-18
1	7	34	-32
2	7	69	64
5	7	47	49
6	7	49	-46
10	7	15	-15
11	7	41	42
15	7	41	-42
18	7	17	18
19	7	17	16
21	7	11	13
22	7	16	-19
25	7	14	-16
0	8	14	-13
1	8	28	-25
2	8	38	-39
3	8	54	-20
4	8	18	-18
5	8	16	-16
6	8	41	40
8	8	66	43
9	8	54	53
11	8	25	24
12	8	61	-65
13	8	39	-60
15	8	13	-15
16	8	26	29
18	8	19	21
1	9	34	34
2	9	31	34
3	9	55	-53
4	9	21	21
5	9	22	-21
6	9	31	30
7	9	49	50
8	9	16	-11
9	9	19	21
10	9	40	-42
13	9	41	-43
14	9	25	24
15	9	23	-25
17	9	36	37
22	9	16	-16
1	10	18	19
2	10	14	-12
4	10	12	-8
6	10	12	9
8	10	16	14
9	10	16	-20
10	10	12	-6
11	10	12	13
13	10	16	18
2	11	46	43
3	11	21	-21
4	11	15	13
5	11	35	35
7	11	13	13
10	11	18	-21
13	11	14	-16
14	11	14	13
15	11	11	-11
16	11	11	10
17	11	14	14
1	12	22	24
3	12	19	19
6	12	14	-16
14	12	14	7
1	13	31	-25
2	13	19	18
3	13	9	6
5	13	36	31
8	13	17	-9
9	13	9	-17
1	14	11	13
3	14	6	4
4	14	6	-5
5	14	13	-7
L=2			
0	0	54	67
1	0	30	-32
2	0	189	-167
3	0	166	-188
4	0	64	-65
5	0	78	-88
6	0	53	-60
7	0	198	188
8	0	16	-10
9	0	96	100
10	0	117	123
12	0	32	-31
13	0	39	43
14	0	54	-57
15	0	82	-78
16	0	32	29
17	0	75	-66
18	0	63	68
19	0	15	22
21	0	16	16
23	0	27	34
26	0	8	-9
27	0	30	-33
1	1	92	-98
2	1	56	-66
3	1	104	100
4	1	115	116
5	1	74	68
7	1	34	-26
8	1	19	-20
10	1	53	-45
11	1	19	-15
12	1	57	49
14	1	39	36
15	1	30	-31
16	1	28	-31
17	1	23	-23
18	1	19	-16
19	1	42	39
21	1	18	19
22	1	10	10
23	1	22	-23
25	1	8	-14
27	1	10	8
0	2	111	-121
1	2	19	28
2	2	42	-37
3	2	31	-37
4	2	36	39
5	2	175	-171
6	2	51	50
7	2	82	75
8	2	61	-53
9	2	131	130
10	2	35	-24
11	2	55	53
12	2	55	57
14	2	22	-18
15	2	120	-119
16	2	29	-32
17	2	19	-11
18	2	25	25
19	2	37	36
20	2	29	54
23	2	11	11
24	2	11	-18
27	2	10	-12
1	3	81	-92
2	3	142	160
3	3	82	82
4	3	11	17
5	3	32	-24
6	3	83	-70
7	3	121	121
8	3	57	-53
9	3	57	50
11	3	86	-87
12	3	39	35
13	3	78	-82
15	3	9	10
16	3	27	-32
17	3	20	19
18	3	10	11
19	3	28	28
21	3	18	21
22	3	9	-10
25	3	31	-32
0	4	51	-48
2	4	31	-29
3	4	89	-84
4	4	81	71
6	4	60	40
7	4	43	43
8	4	18	-15
9	4	8	9
10	4	57	-52
11	4	18	19
12	4	14	-13
14	4	25	28
15	4	10	-14
17	4	34	-37
20	4	14	-15
21	4	14	18
24	4	12	7
1	5	114	-127
2	5	31	25
3	5	78	70
4	5	27	-25
5	5	62	59
6	5	13	-11
7	5	55	59
8	5	26	24
9	5	52	445
10	5	75	-80
11	5	83	-86
12	5	10	-13
13	5	53	-52
14	5	11	8
18	5	16	16
19	5	44	44
20	5	11	-18
21	5	19	25
23	5	30	-32
0	6	66	-64
1	6	28	-25
2	6	22	18
3	6	8	12
4	6	31	27
5	6	42	35
7	6	21	-21
8	6	23	-18
13	6	19	21
16	6	16	20
18	6	14	-18
1	7	77	-80
2	7	29	-24
3	7	46	43
5	7	55	58
6	7	60	60
7	7	49	55
9	7	15	16
10	7	18	-17
11	7	62	-58
12	7	33	-30
13	7	34	-34
16	7	18	18
19	7	25	26
21	7	13	16
22	7	22	-27
23	7	13	-17
0	8	25	25
1	8	16	12
2	8	30	29
3	8	43	40
4	8	17	-17
5	8	45	40
6	8	35	-37
7	8	49	-50
8	8	19	20
9	8	17	-18
10	8	15	13
13	8	28	-30
15	8	36	33
16	8	22	-27
17	8	19	20
19	8	9	-10
20	8	15	15
22	8	7	-7
23	8	10	-12
2	9	54	50
3	9	21	-25
6	9	21	-22
7	9	31	32
9	9	27	28
10	9	16	18
11	9	30	-37
13	9	32	-31
14	9	11	-12
15	9	11	10
17	9	12	15
0	10	34	36
1	10	21	-23
2	10	26	25
3	10	26	26
4	10	35	-30
5	10	56	48
6	10	28	-29
7	10	20	-21
8	10	26	24
9	10	38	-32
10	10	13	18
11	10	25	-24
12	10	11	-11
15	10	35	36
17	10	13	13
19	10	19	-20
2	11	27	19
5	11	16	19
7	11	10	-10
8	11	23	-22
9	11	14	-17
11	11	13	18
12	11	10	12
15	11	11	-13
18	11	11	-12
19	11	4	4
0	12	27	-24
1	12	15	17
3	12	46	40
4	12	39	29
7	12	41	-32
8	12	27	-24
12	12	12	12
13	12	9	-12
14	12	12	13
15	12	5	7
1	13	23	24
3	13	22	-21
4	13	9	11
5	13	10	-7
6	13	16	-16
10	13	18	18
L=3			
1	1	45	-38
2	1	196	-199
3	1	34	-21
4	1	85	85
5	1	87	91
6	1	39	36
7	1	72	73
8	1	38	32
9	1	18	28
10	1	65	59
11	1	43	-30
13	1	107	-97
15	1	60	-54
16	1	16	12
17	1	36	38
18	1	39	-36
19	1	47	56
21	1	15	12
22	1	41	38
23	1	18	-25
24	1	15	-14
25	1	21	-25
26	1	8	-7
30	1	9	-8
0	2	15	-10
1	2	48	45
2	2	21	-19
3	2	112	116
4	2	13	-11
5	2	24	22
6	2	84	77
7	2	89	-87
8	2	27	-30
9	2	80	-78
10	2	34	-34
11	2	18	-20
12	2	57	47
13	2	52	50
14	2	48	-45
15	2	28	25
16	2	14	-15
17	2	12	-16
18	2	25	22
24	2	8	-13
26	2	7	-7
28	2	6	10
1	3	98	-104
3	3	35	34
4	3	20	-13
5	3	91	92
6	3	65	-58
7	3	59	58
9	3	25	-27
10	3	66	60
11	3	60	-56
12	3	8	-12
13	3	14	-15
14	3	35	-31
15	3	9	-8
17	3	15	14
19	3	22	23
22	3	16	17
25	3	7	-12
29	3	5	7
30	3	8	-9
0	4	23	20
1	4	75	72
2	4	58	-63
3	4	94	98
4	4	54	-62
5	4	28	27
6	4	69	68
7	4	31	-31
8	4	9	6
9	4	91	-97
10	4	9	6
11	4	35	-34
13	4	40	41
14	4	61	-67
15	4	26	26
16	4	61	57
17	4	25	26
18	4	38	37
20	4	26	-28
21	4	22	-21
22	4	13	14
23	4	9	-12
26	4	10	-13
27	4	9	11
29	4	7	10
1	5	54	-54
2	5	68	-64
5	5	46	49
6	5	62	61
7	5	30	27
8	5	25	-23
9	5	26	-28
10	5	47	-45
11	5	29	-29
14	5	36	-32
15	5	29	27
18	5	24	13
19	5	17	-19
22	5	12	13
26	5	10	-12
28	5	4	-4
0	6	65	-71
2	6	49	-49
3	6	25	27
4	6	54	68
5	6	49	63
6	6	67	71
7	6	21	17
8	6	66	-67
9	6	58	-55
10	6	20	-22
11	6	68	-72
12	6	55	57
14	6	29	-29
15	6	50	54
16	6	16	-19
17	6	31	36
18	6	25	22
20	6	13	17
21	6	33	-31
23	6	15	-15
24	6	11	-14
26	6	8	-12
27	6	9	9
28	6	8	13
1	7	34	28
2	7	69	75
4	7	27	-28
5	7	35	-32
6	7	13	-10
7	7	20	-20
11	7	13	13
13	7	14	12
17	7	7	-12
18	7	24	24
22	7	27	-27
0	8	31	31
1	8	16	17
2	8	21	-19
3	8	36	32
5	8	8	9
6	8	33	31
7	8	9	-12
8	8	17	14
9	8	17	-19
10	8	11	-9
11	8	27	-27
12	8	18	-20
14	8	7	-8
15	8	22	22
17	8	30	25
18	8	7	9
20	8	12	-11
21	8	18	-21
1	9	34	33
2	9	14	14
4	9	31	-28
5	9	66	-72
6	9	33	33
7	9	22	-26
9	9	31	29
10	9	56	-63
13	9	8	9
14	9	31	27
17	9	8	7
0	10	23	-20
1	10	24	25
3	10	24	27
4	10	27	26
6	10	11	-8
7	10	28	-21
8	10	14	-11
9	10	20	-17
10	10	10	11
16	10	13	-10
20	10	4	9
1	11	21	18
2	11	22	20
5	11	14	-15
7	11	34	-30
10	11	22	-20
11	11	24	-21
13	11	21	18
17	11	4	-12
18	11	11	12
1	12	6	4
2	12	7	9
3	12	10	12
6	12	18	-17
7	12	18	-17
11	12	17	13
15	12	7	5
2	13	18	17
6	13	4	-8
7	13	7	-12
L=4			
0	0	18	-18
1	0	19	-16
3	0	43	-36
5	0	53	46
6	0	55	46
7	0	67	63
8	0	133	112
9	0	111	-110
10	0	17	10
11	0	121	-112
12	0	90	-95
13	0	73	72
14	0	68	-68
15	0	55	53
16	0	17	-12
18	0	29	25
20	0	47	53
21	0	13	-14
22	0	16	-20
1	1	32	-33
2	1	74	68
3	1	44	41
4	1	62	58
6	1	43	-59
7	1	48	-51
8	1	41	-37
10	1	16	14
11	1	19	13
12	1	12	-8
13	1	69	41
16	1	12	12
17	1	29	-26
18	1	13	-14
19	1	14	17
0	2	92	-105
1	2	52	51
3	2	88	84
4	2	24	18
5	2	32	-45
6	2	28	23
8	2	98	101
9	2	34	-32
11	2	35	-30
12	2	89	-88
13	2	36	36
14	2	19	-17
15	2	21	-21
16	2	20	18
17	2	35	34
18	2	21	20
19	2	19	15
20	2	19	18
21	2	29	-28
1	3	42	47
2	3	55	55
3	3	14	10
4	3	119	120
5	3	126	-136
7	3	32	30
8	3	96	-95
9	3	45	40
10	3	13	-12
11	3	12	-7
12	3	13	16
14	3	35	35
15	3	34	35
16	3	29	31
18	3	15	-19
19	3	23	-24
0	4	76	-96
1	4	38	37
2	4	30	-33
4	4	50	45
5	4	30	24
6	4	43	42
8	4	16	10
9	4	40	-39
10	4	35	-36
12	4	27	-27
13	4	14	14
14	4	21	21
15	4	20	21
16	4	17	17
17	4	13	-10
1	5	8	10
3	5	34	39
4	5	90	95
5	5	43	-40
6	5	47	47
7	5	49	-46
8	5	48	-46
9	5	18	16
10	5	29	-26
12	5	16	-15
13	5	31	34
14	5	22	23
15	5	21	17
16	5	56	58
17	5	33	-33
20	5	26	-23
0	6	37	35
2	6	20	-20
3	6	15	12
4	6	15	-12
6	6	29	28
7	6	28	-26
8	6	21	-22
9	6	18	13
10	6	12	-13
11	6	12	10
13	6	21	-17
1	7	12	-13
2	7	14	-9
3	7	45	43
4	7	43	43
5	7	25	-25
6	7	20	18
10	7	21	-24
13	7	33	35
14	7	17	21
16	7	36	49
17	7	24	-27
0	8	72	77
2	8	13	10
3	8	15	-15
4	8	49	-50
6	8	41	-33
7	8	20	-17
9	8	20	23
10	8	25	26
11	8	26	27
12	8	17	20
13	8	32	-34
1	9	20	20
3	9	16	-15
4	9	14	17
5	9	14	-12
7	9	13	-13
8	9	19	-20
9	9	18	16
10	9	18	-24
3	10	28	-31
4	10	32	-27
5	10	15	21
6	10	21	-21
7	10	10	14
8	10	24	-24
10	10	19	18
12	10	38	33
2	11	21	29
5	11	19	15
6	11	9	-14
7	11	16	-14
9	11	13	-15
11	11	14	20
12	11	14	17
13	11	8	7
0	12	14	18
5	12	10	-9
7	12	15	-15
8	12	14	-17
9	12	15	19
12	12	14	14
13	12	11	-12
1	13	13	13
3	13	15	-19
4	13	9	-12
L=5			
1	1	44	43
2	1	45	44
3	1	80	-80
4	1	87	86
7	1	32	25
8	1	48	-44
9	1	13	-12
10	1	80	-72
11	1	55	49
12	1	41	-36
13	1	26	-26
14	1	40	38
15	1	37	-35
16	1	47	47
17	1	41	36
20	1	28	-24
22	1	18	-13
24	1	12	-9
25	1	16	-11
26	1	10	11
28	1	15	12
0	2	37	41
1	2	73	83
2	2	41	48
3	2	52	64
4	2	32	-29
5	2	34	-31
6	2	56	-33
7	2	26	-26
8	2	22	-14
10	2	16	20
11	2	27	27
12	2	39	36
13	2	27	26
15	2	20	21
17	2	17	-15
18	2	16	-13
19	2	19	21
20	2	15	-16
21	2	11	-8
23	2	7	-6
24	2	7	8
25	2	6	8
27	2	11	-8
1	3	10	6
2	3	67	82
3	3	29	-24
4	3	56	62
5	3	20	19
6	3	21	-19
7	3	33	33
8	3	34	-30
9	3	25	-21
11	3	17	-13
12	3	15	13
14	3	8	-10
16	3	20	18
17	3	19	16
18	3	21	25
19	3	13	-15
20	3	13	-13
21	3	12	-13
22	3	26	-24
23	3	20	17
24	3	13	-7
26	3	10	11
27	3	8	-8
0	4	123	134
1	4	49	56
2	4	37	45
3	4	10	-9
4	4	74	-79
5	4	21	-16
6	4	37	-33
7	4	49	48
9	4	46	-66
10	4	11	10
11	4	23	-21
12	4	21	21
13	4	45	41
18	4	30	-31
19	4	11	11
20	4	11	-34
21	4	9	-9
24	4	16	16
26	4	15	12
1	5	41	-48
2	5	26	30
3	5	35	32
4	5	8	11
5	5	31	34
7	5	27	-26
9	5	35	-35
13	5	26	25
14	5	15	17
17	5	18	-17
18	5	8	-12
0	6	27	32
1	6	26	23
2	6	35	37
3	6	21	-15
4	6	11	11
5	6	30	-25
6	6	35	-37
7	6	42	43
8	6	55	-56
11	6	27	-26
12	6	55	57
14	6	22	30
16	6	17	-18
17	6	18	16
18	6	32	-29
19	6	20	20
20	6	16	-14
21	6	27	-23
22	6	6	7
23	6	7	-8
24	6	9	8
1	7	11	11
2	7	24	21
3	7	8	5
4	7	27	-27
5	7	34	-36
6	7	25	-21
8	7	14	11
9	7	46	34
10	7	42	40
11	7	24	-20
14	7	33	-25
15	7	19	17
16	7	12	-8
17	7	7	-8
18	7	11	13
1	8	30	-17
2	8	14	11
3	8	22	-24
4	8	21	-23
5	8	10	13
6	8	36	-28
7	8	34	35
11	8	33	-25
12	8	10	8
13	8	17	13
14	8	16	15
16	8	7	6
18	8	11	-10
20	8	21	-19
2	9	34	-43
3	9	20	23
4	9	38	-32
5	9	33	-38
6	9	34	23
7	9	15	-13
8	9	30	25
9	9	39	33
14	9	13	-11
17	9	18	-13
19	9	13	14
0	10	17	13
3	10	16	15
7	10	16	-16
8	10	10	-10
10	10	14	12
12	10	10	9
2	11	16	-14
3	11	9	11
4	11	25	-20
5	11	12	-11
8	11	21	19
9	11	11	10
10	11	17	15
11	11	10	-8
3	12	16	12
L=6			
0	2	40	40
0	4	33	-44
0	6	8	-6
0	8	41	41
0	0	11	-19
L=7			
0	2	15	-16
0	4	30	-48
0	6	53	-44
0	8	11	-16
L=8			
0	0	32	27
0	2	36	35
0	4	22	-24
0	6	7	5
L=9			
0	4	25	27
0	6	32	-28
0	8	31	-28
L=10			
0	4	19	-18

[a] The running index is L. The sequence is H, K, F_o, and F_c; F(000) = 1184.

phine)nickel[9]). The compound should be formulated as ionic. This is consistent with its good solubility in polar solvents and poor solubility in nonpolar solvents as reported by Guerrieri.[2] The molecular ion π-C_3H_5-$Ni(SC(NH_2)_2)_2^+$ shows a distorted square-planar arrangement of the ligands around the metal atom. The Ni–S interatomic distances are in accordance with those found in a number of diamagnetic square-planar nickel complexes (*cf.* ref 10–14, for example). The S(1)NiS(2) angle, which would be 90° in a regular square-planar model, is distorted to about 110°. Both the thiourea groups are equally involved in this phenomenon (S(1)–C(3) = 3.00 (2) Å; S(2)–C(1) = 2.95 (2) Å). The distortion observed is definitely larger than any possible experimental error. Interactions between the metal atom and the π electrons of the S=C groups as well as hydrogen bonding between the $-NH_2$ groups and the chlorine ions or simply nonbonded repulsion between the two thiourea groups could be involved. Other cases of similar distortions of comparable magnitude in nickel complexes containing thiourea as ligand have been observed.[8,15] It seems that hydrogen bonding is the driving force for the opening of the

---

(9) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

(10) L. Cavalca, M. Nardelli, and G. Fava, *Acta Crystallogr.*, **15**, 1139 (1962).

(11) J. F. McConnel and V. Kastalsky, *ibid.*, **22**, 853 (1967).

(12) P. L. Jones, G. B. Ansell, and L. Katz, *Chem. Commun.*, 78 (1968).

(13) M. Bonamico, G. Dessy, and V. Fares, *ibid.*, 324 (1969).

(14) H. Luth, E. A. Hall, W. A. Spofford, and E. L. Amma, *ibid.*, 520 (1969).

(15) M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, **8**, 424 (1969).

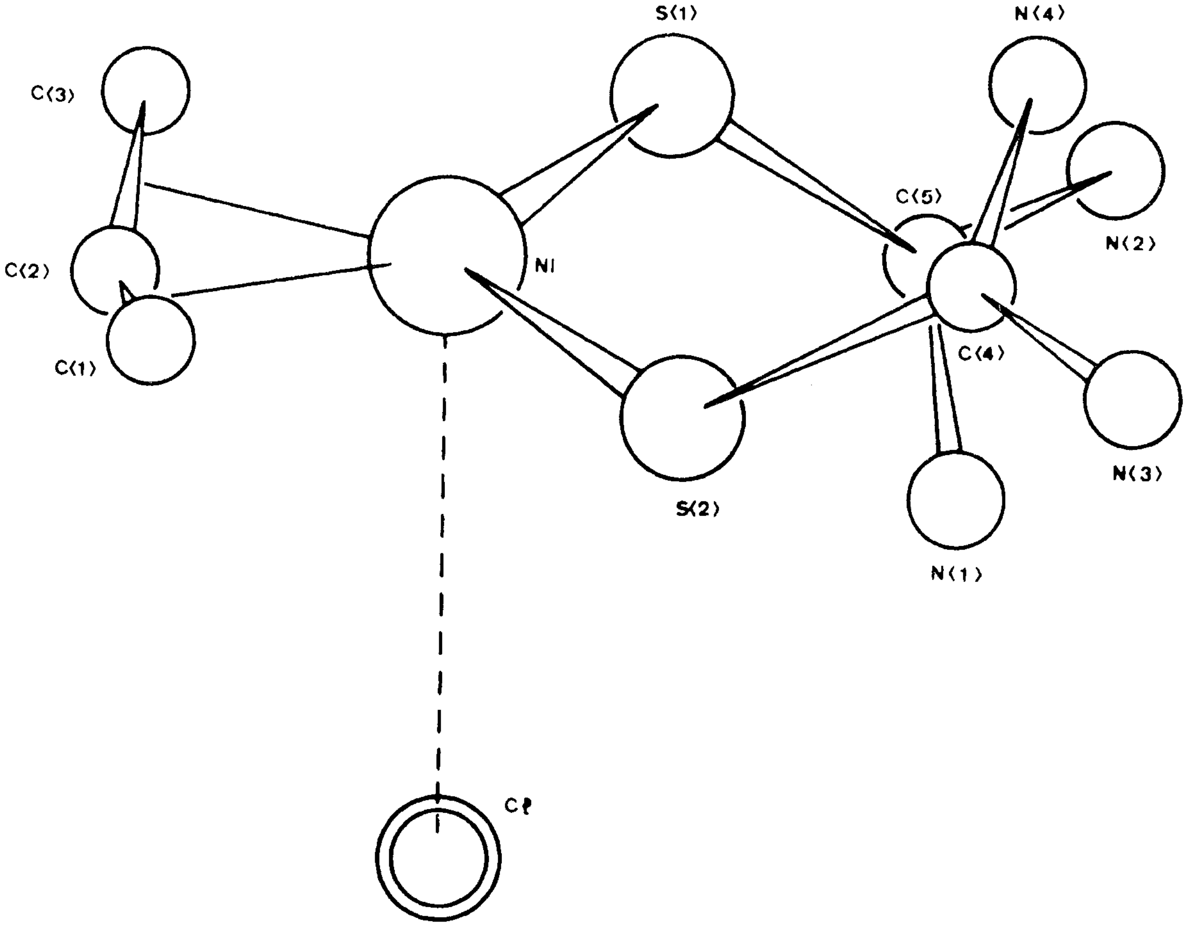


Figure 1.—Molecular model of the ionic couple π-$C_3H_5Ni(SC(NH_2)_2)_2{}^+,Cl^-$. The hydrogen atoms are not shown.

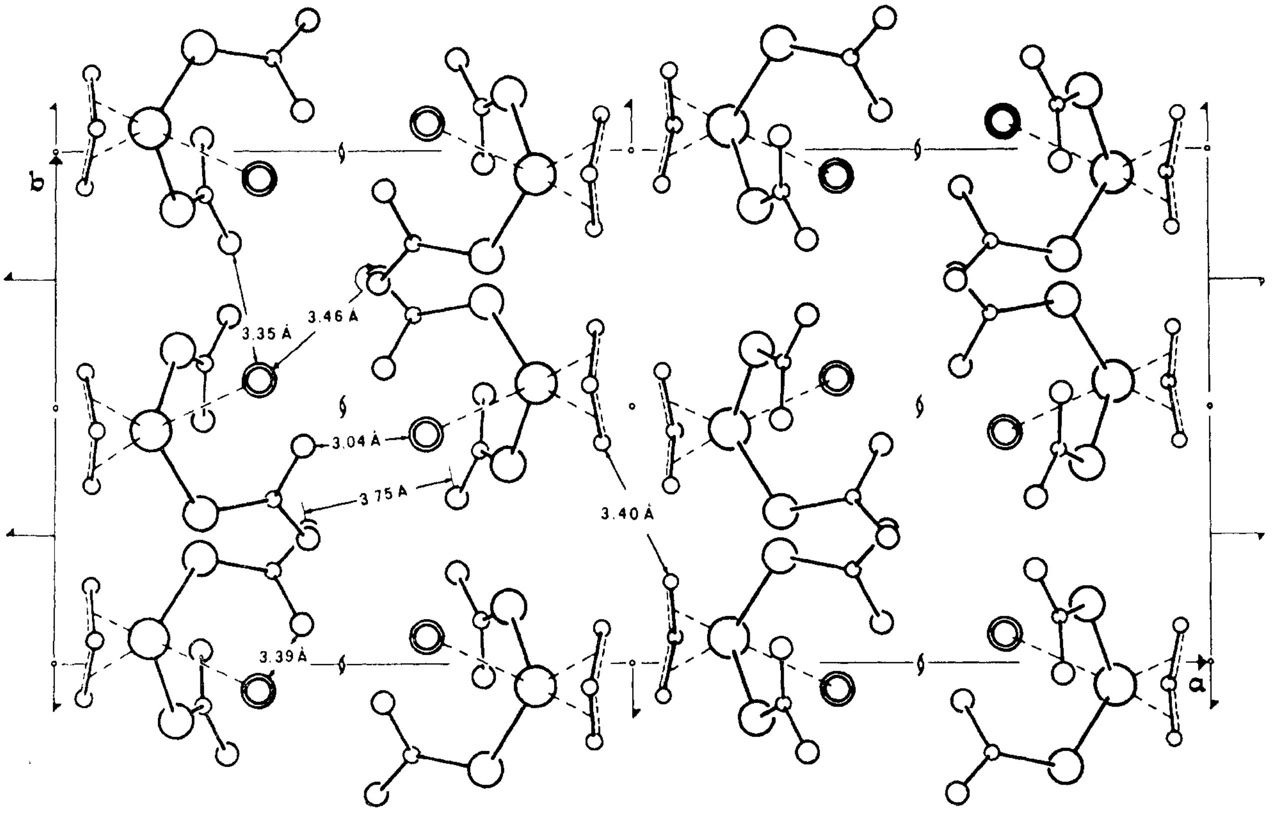


Figure 2.—Content of the unit cell viewed along the crystallographic *c* axis.

TABLE IV[a]

Molecular Parameters and Significant Nonbond Distances, Å

Ni–Cl	3.445 (4)	S(1)–N(4)	3.39 (1)
Ni–S(1)	2.218 (4)	S(1)–N(3)	5.17 (1)
Ni–S(2)	2.212 (4)	S(1)–C(4)	3.90 (1)
Ni–C(1)	2.04 (2)	S(2)–N(1)	3.45 (1)
Ni–C(2)	1.97 (3)	S(2)–N(2)	5.13 (2)
Ni–C(3)	2.07 (2)	N(1)–N(4)	3.50 (2)
C(1)–C(2)	1.40 (3)	N(1)–N(3)	4.27 (2)
C(2)–C(3)	1.33 (3)	N(1)–C(4)	3.49 (2)
S(1)–C(5)	1.72 (1)	N(2)–N(3)	5.38 (2)
C(5)–N(1)	1.35 (2)	N(2)–N(4)	3.80 (2)
C(5)–N(2)	1.34 (2)	N(2)–C(4)	4.35 (2)
S(2)–C(4)	1.71 (1)	N(3)–C(5)	4.71 (2)
C(4)–N(3)	1.35 (2)	N(4)–C(5)	3.25 (2)
C(4)–N(4)	1.34 (2)		
Cl–S(2)	3.872 (6)		
Cl–N(1)	3.39 (1)		

Angles, Deg

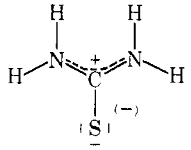
S(1)NiS(2)	110.9 (1)	S(1)C(5)N(2)	120.2 (3)
ClNiS(1)	96.3 (1)	N(1)C(5)N(2)	122.0 (3)
ClNiS(2)	83.3 (1)	NiS(2)C(4)	116.1 (5)
C(1)C(2)C(3)	123.9 (10)	S(2)C(4)N(3)	118.3 (2)
NiS(1)C(5)	112.0 (4)	S(2)C(4)N(4)	123.2 (3)
S(1)C(5)N(1)	116.1 (4)	N(3)C(4)N(4)	118.5 (6)

Internal Rotation Angles, Deg

NiS(1)C(5)N(1)	18.4 (8)	S(1)NiS(2)C(4)	29.4 (10)
NiS(2)C(4)N(4)	5.2 (8)	S(2)NiS(1)C(5)	35.7 (10)

[a] Standard deviations are given in parentheses.

Cl–Ni–S angle from 90° to 96.7° in dichlorotetrakis(thiourea)nickel,[8] while nonbonded interactions between thiourea groups might be mostly responsible for the nonregularity of the octahedral structure of hexakis(thiourea)nickel bromide.[15] A list of intramolecular nonbonded distances between thiourea groups in π-allyldi(thiourea)nickel chloride is reported in Table IV. These distances indicate that repulsion between the thiourea ligands should be considerable in this structure. The Ni–S–C angles are both less than 120°. This would be the expected value if the sulfur were bonded to the metal atom with a filled sp^2 nonbonding orbital, but this seems to be too simple a picture. The lessening from 120° of the MSC angle is constantly observed in thiourea-containing metal complexes, not only in those already referred to and containing nickel as central atom but also in those containing copper,[16] zinc,[17] or cadmium.[18] Some explanation could be given considering for the thiourea groups the contribution of an electronic structure involving sp^3 hybridization on the sulfur atom and π bonding between carbon and nitrogen



Such a structure implies the planarity of the $C(NH_2)_2$ groups, as appears to be the case in the complex hexakis(thiourea)nickel bromide,[15] and makes conversely more acceptable the nonplanarity of the MSCN groups which is observed in various degrees in the above mentioned complexes as well as in that presented here.

As far as the allyl ligand is concerned, the carbon–carbon bond lengths should be considered equal within experimental error. The dihedral angle between the plane containing the carbon atoms of the allyl group and that containing the Ni, S_1, and S_2 atoms is 118 ± 3°. A dihedral angle of 106° is found in dimeric 2-carboxyethyl-π-allylnickel bromide;[19] the same value was calculated theoretically by Kettle and Mason.[20]

Although the difference between these values does not allow much speculation if compared with calculated errors, one should observe that the geometrical features of the allyl-to-metal bonding can be influenced by steric factors both intermolecular, as is claimed by Smith[21] for $(\pi\text{-}C_3H_5PdCl)_2$, and intramolecular, as seems to occur in bis(1,2-diphenylphosphine)ethane-π-methallylnickel bromide[22] where repulsion between the equatorial methallyl ligand and the apical bromine is presumably significant. The crystal structure appears to be determined by the formation of efficient hydrogen bonds between the NH_2 groups and the chlorine ions. This fact is by no means peculiar to this structure but is of constant occurrence in the solid-state structures of thiourea-containing metal complexes. The relevant N–Cl distances are given in Figure 2, which also shows the content of the unit cell viewed along the *c* axis.

Acknowledgment.—The author is grateful to Dr. F. Guerrieri and Dr. G. P. Chiusoli for furnishing crystals of the compound, to Dr. A. Immirzi for the use of his computer programs, and to Professor P. Corradini for encouragement and advice. The technical assistance given by Mrs. A. Hermann is also gratefully acknowledged.

---

(16) Y. Okaya and C. B. Knobler, *Acta Crystallogr.*, **17**, 928 (1964).

(17) N. R. Kunchor and M. R. Truter, *J. Chem. Soc.*, 3478 (1958).

(18) L. Cavalca, P. Damiano, G. F. Gasparri, and P. Boldrini, *Acta Crystallogr.*, **22**, 878 (1967).

(19) M. R. Churchill and T. A. O'Brien, *Inorg. Chem.*, **7**, 1386 (1967).

(20) S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, **5**, 573 (1966).

(21) A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965).

(22) M. R. Churchill and T. A. O'Brien, *Chem. Commun.*, 246 (1968).