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The Crystal Structure of Dichloro-(acetonethiosemicarbazone)zinc(II)

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The crystal structure of dichloro-(acetonethiosemicarbazone)zinc(II) has been determined from three dimensional X-ray diffraction data collected on a General Electric XRD-6 automatic diffractometer using Cu-Kα radiation and the stationary crystal-stationary counter technique. The monoclinic cell has dimensions of $a=7.823(2)$ Å, $b=14.310(2)$ Å, $c=8.691(2)$ Å, and $\beta=100.32(2)°$. The space group is $P2_1/n$ and, with 4 molecules per unit cell, D_c is 1.855 g/cm^3 and D_m is 1.85 g/cm^3. The structure was determined by the heavy atom method and refined by full matrix least-squares techniques to a final R of 0.045 for the 1322 observed reflections used in the analysis. The zinc atom is in the center of a distorted tetrahedron with Zn-Cl distances of 2.203(2) and 2.252(2) Å. The Zn-S distance of 2.303(2) and the Zn-N distance of 2.116(4) Å complete the tetrahedron. The difference in the two Zn-Cl distance appears to result from hydrogen bonding to only one Cl atom.

Introduction

A series of α–(N)heterocyclic thiosemicarbazones able to act as univalent tridentate N–N–S ligands was found to have carcinostatic activity.[2] Confirmation of the tridentate nature of two thiosemicarbazones which have antitumor properties was provided by X-ray crystal structure studies of their nickel complexes.[3] To compare the chelating ability of an inactive thiosemicarbazone, acetone thiosemicarbazone [ATSC is $SC(NH_2)NHN:C(CH_3)_2$] was prepared and the adduct with nickel chloride was studied. When the $NiCl_2 \cdot (ATSC)_2$ complex was found to be pentacoordinated,[4] our studies were extended to other metal halides. The zinc chloride-ATSC complex was chosen for a crystal structure analysis since it would provide an interesting comparison with other $ZnCl_2$ base-adduct structures which were summarized recently.[5] A particularly interesting comparison would be with the $Cl_2Zn \cdot TSI$ complex,[6] TSI is thiosemicarbazide, because of the close similarities between TSI and thiosemicarbazones.

Experimental Section

The compound was prepared by mixing hot ethanolic solutions of zinc chloride and ATSC (mole ratio of 1:1) from which the complex separates on cooling.[7] Recrystallization from hot ethanol gave long, colorless needles of dichloro-(acetonethiosemicarbazone)-zinc(II), $ZnCl_2$ (ATSC). Preliminary precession and Weissenberg photographs indicated monoclinic symmetry. The systematic absences of h0l absent if $h+l=2n+1$ and 0k0 absent if $k=2n+1$ indicated the most probable space group to be $P2_1/n(C_{2}{}^{5}h)$.

A small needle with a cross-section of 0.12×0.15 mm was cut to a length of 0.15 mm and then dissolved with alcohol to approximate a sphere of 0.10 mm in diameter. This crystal was then used for the measurement of the intensities. The unit cell dimensions were determined by a least-squares fit of 15 two-theta values (in the range of 25-40°) measured for the CuK_β ($\lambda=1.39217$ Å) peak. The final values with their estimated standard deviations are $a=7.823(2)$ Å, $b=14.310(5)$ Å, $c=8.691(2)$ Å, and $\beta=100.32(2)°$. The density calculated for 4 molecules of $ZnCl_2C_4H_9N_3S$, M.W. 267.48 per unit cell is 1.855 g/cm^3, in good agreement with the value measured by flotation of 1.85 g/cm^3.

Intensity data were measured with a General Electric XRD-6 diffractometer using CuKα, ($\lambda=1.54051$ Å) radiation, with a take-off angle of 4°. A 0.35 mil Ni foil was placed in front of the counter window. All the reflections in the hemisphere with $2\theta<135°$ were measured twice (a 20 sec count was taken with the crystal and counter stationary) for a total of 6750 measurements. A set of 4 standard reflections were measured after every 100 reflections and showed only a slight variation (maximum 1%) over the period of intensity measurements. The background was measured at various points in reciprocal space free from any reflections and was used to derive a background curve as a function of two-theta. A total of 1732 unique reflections was obtained after averaging intensity measurements equivalent by symmetry. The 1322 reflections that were greater than 1.2 times the

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[1] Research performed at the Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.
[2] F.A. French and E.J. Blanz, Jr., *J. Med. Chem.*, *9*, 585 (1966).
[3] (a) M. Mathew and G.J. Palenik, *J. Am. Chem. Soc.*, *91*, 6310 (1969) (b) G.R. Clark, R. Restivo, and G.J. Palenik, The structure of bis(2-formylpyridine thiosemicarbazonato)nickel(II) has been determined and is similar to that found in 3a.
[4] M. Mathew and G.J. Palenik, *J. Am. Chem. Soc.*, *91*, 4923 (1969).
[5] H.S. Preston and C.H.L. Kennard, *J. Chem. Soc.* (A), 1956 (1969).
[6] L. Cavalca, M. Nardelli, and G. Branchi, *Acta Cryst.*, *13*, 688 (1960).
[7] A.V. Ablov and N.V. Gerbeleu, *Russ. J. Inorg. Chem.*, *9*, 46 (1964).

Table I. Final parameters ($\times 10^4$) for the non-hydrogen atoms. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+\beta_{12}hk+\beta_{13}h\ell+\beta_{23}\ell)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	1728(1)	338(1)	2347(1)	174(2)	30(1)	79(1)	17(2)	12(2)	24(1)
Cl1	—778(3)	986(1)	1342(2)	204(4)	57(1)	138(3)	86(3)	—35(5)	34(3)
Cl2	3950(2)	1093(1)	1565(2)	195(3)	38(1)	75(2)	—33(3)	24(4)	22(2)
S	2014(2)	—1257(1)	2647(2)	212(4)	23(1)	68(2)	— 2(3)	— 7(4)	—10(2)
N1	2366(6)	384(3)	4817(5)	176(10)	29(2)	52(6)	— 3(9)	43(12)	9(7)
N2	3066(7)	—457(3)	5443(5)	178(10)	27(2)	67(6)	22(9)	—23(12)	21(7)
N3	3670(8)	—1992(4)	5264(6)	281(15)	26(3)	100(8)	5(10)	—40(17)	10(7)
C1	2975(8)	—1230(4)	4577(7)	167(13)	21(3)	87(8)	— 6(9)	0(16)	0(8)
C2	2347(8)	1084(4)	5753(7)	165(12)	26(3)	81(8)	—17(10)	102(16)	—17(8)
C3	3062(10)	1069(5)	7456(8)	238(17)	42(3)	106(9)	—15(13)	23(21)	—35(10)
C4	1585(10)	1969(4)	5034(8)	239(16)	24(3)	152(10)	12(12)	86(22)	31(10)

Table II. Positional parameters ($\times 10^3$) and the isotopic thermal parameters of the hydrogen atoms.

Atom	Bonded to	x	y	z	β(Å^2)
H1	N2	366	— 44	651	3.0
H2	N3	442	—193	629	3.5
H3	N3	346	—257	465	3.5
H4	C3	438	91	774	4.5
H5	C3	268	54	790	4.5
H6	C3	342	171	778	4.5
H7	C4	124	188	369	4.5
H8	C4	60	220	557	4.5
H9	C4	228	250	537	4.5

background were considered to be observed and were used in the analysis. The remaining 410 reflections were given a value of 0.1 times the appropriate background and were identified by a negative value for the intensity. An empirical correction for the α_1—α_2 splitting was made; these data were then reduced to a set of observed amplitudes on an arbitrary scale by application of Lorentz-polarization corrections. No absorption corrections were made because although the value of μ was 101.0 cm^{-1} the variation was only about 8% (μr is 0.5).

Structure Determination and Refinement

The positions of the Zn, Cl, and S atoms were determined from a sharpened three-dimensional Patterson function. A Fourier synthesis computed on the basis of these atoms (the Cl and S atoms were treated as S atoms initially) was used to locate the remaining non-hydrogen atoms. Three least-squares cycles using individual isotropic thermal parameters reduced R, the usual residual, to 0.13. An additional three least-squares cycles with anisotropic thermal parameters for all atoms reduced R to 0.052. A difference Fourier synthesis was used to locate all the hydrogen atoms with no other significant peaks being found in this synthesis. The contributions of the hydrogen atoms were included in all subsequent calculations but their parameters were not refined. Two additional least-squares cycles reduced R to 0.045 and all the shifts were less than 1/10 of an estimated standard deviation so that the refiniment was terminated. The final parameters and their estimated standard deviations for the non-hydrogen atoms are tabulated in Table I. The hydrogen parameters used in the calculations are given in Table II. The observed and calculated structure amplitudes are given in Table III.

The quantity minimized in the least-squares calculations was $\Sigma w(|F_o|-|F_c|)^2$ with the full matrix being computed for each cycle The weighting scheme used was:

$$\begin{aligned}\sqrt{w} &= |F_o|/4F\text{min} \text{ if } |F_o|<4F\text{min}\\ &=1 \text{ if } 4F\text{min} <|Fo|<6F\text{min}\\ &=6F\text{min}/|F_o| \text{ if } |F_o|>6F\text{min}\end{aligned}$$

where Fmin was the nominally minimum observable F_o which in this case was 5.5 on the same scale as Table III. The scattering factors were taken from the International Tables for X-ray Crystallography,[8] with the value for zinc being corrected for the real part of the anomalous dispersion correction.[9] All the calculations were carried out on an IBM 360-Model 75 computer using programs written or modified by one of us(GJP).

Discussion

The atomic numbering and pertinent bond distances are illustrated in Figure 1, with the bond angles tabulated in Table IV. The zinc atom is at the center of a severely distorted tetrahedron with the two Cl atoms and the N and S atoms of the ATSC molecule at the apices. The angles involving the Zn atom range from 85.2 to 121.5° and illustrate the distortions from tetrahedral symmetry. The smallest angle, S—Zn—N1, is undoubtably a consequence of the five-membered chelate ring system involving the ATSC

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(8) *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, England (1962), p. 202.
(9) D. Cromer, *Acta Cryst.*, *18*, 17 (1965).

Table III. Observed and calculated structure amplitudes (× 10) for dichloro-(acetonethiosemicarbazone)zinc(II).

H	FO	FC
K= 0, L= 0		
2	1362	-1430
4	410	-415
6	112	119
8	219	-193
K= 0, L= 1		
-9	130	-114
-7	155	147
-5	432	-427
-3	326	-319
-1	1200	1443
1	867	-882
3	147	137
5	491	509
7	249	-249
9	-30	-9
K= 0, L= 2		
-8	287	304
-6	223	-216
-4	198	-160
-2	554	-514
0	892	-898
2	1066	1049
4	652	655
6	348	-355
8	55	75
K= 0, L= 3		
-9	167	166
-7	246	-224
-5	117	106
-3	-27	3
-1	1119	-1114
1	1158	1209
3	223	-216
5	257	-257
7	234	240
K= 0, L= 4		
-8	251	-270
-6	458	487
-4	362	364
-2	1027	-1055
0	551	567
2	1093	-1112
4	70	-83
6	473	465
K= 0, L= 5		
-7	341	342
-5	-40	22
-3	416	-393
-1	452	454
1	944	-945
3	-37	55
5	141	135
7	123	-120
K= 0, L= 6		
-8	170	151
-6	353	-329
-4	56	-93
-2	821	840
0	314	-310
2	156	170
4	254	-254
6	228	-222
K= 0, L= 7		
-7	326	-253
-5	210	206
-3	429	433
-1	428	-415
1	217	206
3	-51	37
5	189	-150
K= 0, L= 8		
-6	205	185
-4	308	-88
-2	566	-556
0	539	508
2	186	188
4	52	-35
K= 0, L= 9		
-5	157	-149
-3	253	-229
-1	451	437
1	111	-110
3	88	83
K= 0, L= 10		
-4	43	43
-2	117	153
0	415	-395
K= 1, L= 0		
1	474	446
2	166	139
3	584	-580
4	124	122
5	395	385
6	-39	25
7	-48	-63
8	112	-118
9	110	-120
K= 1, L= 1		
-9	57	59
-8	139	136
-7	-47	-27
-6	180	175
-5	139	-140
-4	1378	-1411
-3	46	-23
-2	1188	1276
-1	113	101
0	292	-257
1	77	-86
2	254	215
3	168	-147
4	689	698
5	132	128
6	338	-328
7	-50	-13
8	181	-165
9	85	78
K= 1, L= 2		
-9	145	133
-8	74	-63
-7	-47	-26
-6	221	227
-5	651	-658
-4	96	-99
-3	797	812
-2	627	619
-1	189	-177
0	771	-776
1	682	-683
2	685	-644
3	877	884
4	258	255
5	254	-260
6	-46	58
7	-52	24
8	120	94
K= 1, L= 3		
-9	-33	-24
-8	-49	-4
-7	134	127
-6	86	-80
-5	58	45
-4	767	766
-3	64	-57
-2	819	-828
-1	178	-147
0	1196	-1272
1	183	169
2	1006	1033
3	174	-111
4	260	-265
5	53	-57
6	259	262
7	-49	57
8	-33	36
K= 1, L= 4		
-9	-31	-25
-8	-44	2
-7	-50	61
-6	132	-125
-5	427	426
-4	57	-25
-3	814	-825
-2	464	451
-1	113	95
0	331	324
1	379	390
2	352	-354
3	480	-495
4	256	-255
5	157	160
6	58	85
7	69	63
K= 1, L= 5		
-8	59	-27
-7	-52	-70
-6	200	203
-5	89	91
-4	453	-445
-3	92	92
-2	913	917
-1	223	215
0	-30	16
1	226	-214
2	658	-622
3	-38	-1
4	179	194
5	-51	45
6	-46	30
7	60	-65
K= 1, L= 6		
-8	-34	45
-7	53	97
-6	-51	-5
-5	216	-225
-4	271	-263
-3	587	585
-2	125	115
-1	140	-135
0	62	36
1	427	-485
2	233	247
3	300	293
4	-50	42
5	-46	-40
6	156	-159
K= 1, L= 7		
-7	-38	-53
-6	276	-240
-5	84	-99
-4	259	262
-3	-43	20
-2	206	-204
-1	-41	21
0	104	105
1	226	225
2	452	426
3	58	-87
4	282	-272
5	99	-82
K= 1, L= 8		
-7	114	-112
-6	-38	-4
-5	175	144
-4	117	108
-3	159	-143
-2	266	-265
-1	148	125
0	-50	54
1	293	295
2	88	-85
3	345	-323
4	52	62
K= 1, L= 9		
-6	188	220
-5	-36	-13
-4	255	-277
-3	101	-144
-2	-48	15
-1	-49	28
0	88	58
1	-41	-8
2	147	-134
3	56	55
K= 1, L= 10		
-4	-30	8
-3	-32	46
-2	148	141
-1	-33	-13
0	62	-63
K= 2, L= 0		
0	1167	1368
1	376	-366
2	655	-655
3	-26	-15
4	63	-61
5	232	236
6	166	165
7	51	85
8	136	-139
9	69	-80
K= 2, L= 1		
-9	-33	-51
-8	89	87
-7	192	188
-6	82	81
-5	271	-264
-4	457	449
-3	157	-159
-2	1443	-1546
-1	812	815
0	488	-470
1	580	-567
2	207	220
3	41	-50
4	580	565
5	381	385
6	116	111
7	196	-199
8	107	-100
K= 2, L= 2		
-9	77	79
-8	165	161
-7	-47	42
-6	322	-329
-5	143	118
-4	276	262
-3	325	-315
-2	142	131
-1	350	-351
0	968	-950
1	-26	25
2	325	323
3	267	158
4	505	506
5	295	-307
6	255	-301
7	151	145
8	-38	29
K= 2, L= 3		
-9	64	58
-8	-48	-43
-7	269	-198
-6	66	-45
-5	225	248
-4	575	564
-3	190	151
-2	237	228
-1	784	-791
0	514	-476
1	506	503
2	286	-287
3	86	93
4	480	-488
5	241	-249
6	245	263
7	167	167
8	114	117
K= 2, L= 4		
-9	-30	-43
-8	133	-121
-7	-51	70
-6	163	158
-5	182	192
-4	300	296
-3	110	101
-2	642	-646
-1	120	-113
0	458	465
1	61	-56
2	287	-282
3	185	-184
4	166	-174
5	152	152
6	281	288
7	100	-108
K= 2, L= 5		
-8	-38	-17
-7	174	167
-6	132	-131
-5	65	-50
-4	135	-130
-3	738	-739
-2	57	107
-1	499	504
0	680	656
1	354	-352
2	100	-83
3	176	-192
4	-44	0
5	261	257
6	298	-293
7	54	-45
K= 2, L= 6		
-8	113	107
-7	146	-126
-6	275	-292
-5	121	-90
-4	59	53
-3	309	320
-2	467	470
-1	64	51
0	368	-368
1	106	-107
2	-40	-49
3	167	170
4	148	151
5	131	-124
6	144	-143
K= 2, L= 7		
-7	164	-142
-6	-45	55
-5	-51	57
-4	-47	-16
-3	270	267
-2	322	-321
-1	202	-300
0	172	-185
1	79	72
2	502	502
3	128	132
4	-46	10
5	153	-203
K= 2, L= 8		
-7	-30	9
-6	-38	6
-5	-47	-79
-4	-52	117
-3	256	-255
-2	390	-333
-1	149	135
0	247	228
1	188	177
2	114	108
3	145	-122
4	154	-165
K= 2, L= 9		
-5	-35	-12
-4	-39	-30
-3	311	-190
-2	174	165
-1	278	277
0	165	-166
1	-39	-56
2	317	-302
3	88	-87
K= 2, L= 10		
-3	-32	6
-2	164	165
-1	137	-138
0	137	-157
K= 3, L= 0		
1	365	361
2	662	635
3	534	-514
4	610	602
5	-36	17
6	118	-118
7	134	130
8	155	-154
9	-30	-33
K= 3, L= 1		
-9	57	91
-8	83	74
-7	-48	42
-6	-40	58
-5	303	-308
-4	251	-247
-3	132	132
-2	517	492
-1	142	-172
0	148	174
1	330	-320
2	654	-691
3	218	214
4	73	78
5	88	74
6	158	163
7	86	-71
8	67	-84
K= 3, L= 2		
-9	-32	61
-8	160	-147
-7	-48	5
-6	329	338
-5	101	-111
-4	312	328
-3	360	367
-2	154	-155
-1	209	-204
0	1065	-1089
1	385	-381
2	168	-151
3	479	481
4	152	155
5	62	-80
6	-46	73
7	229	-227
8	184	170
K= 3, L= 3		
-9	69	-66
-8	107	-58
-7	176	180
-6	-42	25
-5	238	244
-4	91	-76
-3	327	-328
-2	123	120
-1	237	-215
0	121	104
1	266	265
2	459	465
3	301	-309
4	258	-311
5	-42	16
6	212	-208
7	-46	37
8	147	149
K= 3, L= 4		
-9	73	-89
-8	-41	-56
-7	-51	-27
-6	-44	-49
-5	146	157
-4	55	-38
-3	142	-155
-2	453	476
-1	-28	-33
0	445	468
1	412	417
2	456	-507
3	252	-305
4	284	-282
5	-46	44
6	-52	41
7	55	93
K= 3, L= 5		
-8	-37	12
-7	-51	-58
-6	239	225
-5	-42	0
-4	413	-419
-3	332	336
-2	61	-56
-1	159	152
0	329	321
1	450	-445
2	186	-192
3	138	185
4	147	166
5	-51	26
6	89	84
7	115	-140
K= 3, L= 6		
-8	-32	22
-7	-44	25
-6	-51	-61
-5	224	-234
-4	59	-55
-3	-38	53
-2	147	-133
-1	236	230
0	-36	43
1	304	-314
2	331	350
3	204	201
4	-51	-3
5	-45	48
6	250	-254
K= 3, L= 7		
-7	70	-28
-6	-48	28
-5	-51	-52
-4	-48	54
-3	-45	-56
-2	140	143
-1	-42	13
0	420	-433
1	351	347
2	204	196
3	151	-147
4	-44	5
5	52	-40
K= 3, L= 8		
-6	-37	61
-5	134	133
-4	105	119
-3	109	-109
-2	332	-329
-1	249	-264
0	-51	42
1	316	303
2	133	-140
3	85	-85
4	154	173
K= 3, L= 9		
-5	90	-100
-4	124	-133
-3	71	-84
-2	-45	-22
-1	-45	-9
0	326	307
1	116	-102
2	211	-200
K= 3, L= 10		
-3	-31	23
-2	85	111
-1	57	120
0	118	-136
K= 4, L= 0		
0	887	-880
1	676	-678
2	120	-125
3	214	215
4	59	-35
5	195	194
6	352	365
7	89	-88
8	-42	8
K= 4, L= 1		
-9	-30	44
-8	102	190
-7	229	225
-6	198	-203
-5	131	-130
-4	181	183
-3	133	-128
-2	165	165
-1	188	193
0	541	-588
1	80	-79
2	249	254
3	213	-207
4	345	349
5	-26	60
6	-44	-47
7	84	-84
8	-34	4
K= 4, L= 2		
-9	67	84
-8	-45	-26
-7	186	-178
-6	255	-257
-5	258	252
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-3	111	121
-2	565	557
-1	741	-730
0	265	314
1	461	453
2	641	-401
3	-30	36
4	144	-135
5	288	-292
6	118	-116
7	247	249
8	-35	73
K= 4, L= 3		
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-8	95	-85
-7	160	-144
-6	106	117
-5	279	284
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-3	269	263
-2	-27	-18
-1	342	-336
0	305	306
1	-27	-21
2	515	-501
3	363	381
4	314	-323
5	316	-327
6	320	325
7	-44	65
8	-30	5
K= 4, L= 4		
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-7	131	134
-6	54	-53
-5	71	-50
-4	121	-121
-3	124	-124
-2	404	-395
-1	580	582
0	566	569
1	445	-441
2	663	641
3	56	-56
4	435	-445
5	120	113
6	-51	3
7	-36	-42
K= 4, L= 5		
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-7	-30	-62
-6	281	-258
-5	161	-162
-4	157	-156
-3	87	-86
-2	409	409
-1	391	393
0	177	-188
1	102	57
2	65	76
3	281	-354
4	-47	-4
5	213	208
6	199	-194
7	-30	22
K= 4, L= 6		
-8	56	66
-7	155	-160
-6	-52	6
-5	-46	32
-4	63	75
-3	213	223
-2	231	-238
-1	248	-245
0	151	-156
1	225	230
2	177	-177
3	73	71
4	499	492
5	244	-236
6	-32	-23
K= 4, L= 7		
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-6	92	110
-5	-52	-104
-4	109	-103
-3	-46	15
-2	240	-230
-1	269	-270
0	167	168
1	80	62
2	154	155
3	300	254
4	56	-88
5	216	-232
K= 4, L= 8		
-6	86	-95
-5	-42	-41
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-3	201	-240
-2	103	-88
-1	284	290
0	-52	-27
1	-51	-46
2	-46	7
3	-38	-31
4	274	-300
K= 4, L= 9		
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-4	74	-86
-3	85	-87
-2	217	243
-1	-43	-57
0	256	-235
1	-37	34
2	37	-61
K= 4, L= 10		
-3	-30	29
-2	68	93
-1	114	-142
K= 5, L= 0		
1	101	104
2	870	-880
3	401	-388
4	643	643
5	-36	39
6	175	-184
7	155	152
8	-39	-48
K= 5, L= 1		
-8	-41	-14
-7	75	84
-6	-43	-31
-5	335	-344
-4	533	525
-3	773	767
-2	389	375
-1	555	-560
0	700	-662
1	383	-392
2	533	-534
3	682	695
4	110	108
5	200	-203
6	236	247
7	85	-78
8	-37	7
K= 5, L= 2		
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-7	-51	38
-6	152	-156
-5	122	118
-4	558	561
-3	284	285
-2	761	-748
-1	161	-168
0	217	203
1	297	-294
2	535	547
3	115	118
4	413	-415
5	-41	22
6	88	78
7	202	-195
8	51	43
K= 5, L= 3		
-8	126	-123
-7	62	-78
-6	143	-145
-5	338	346
-4	78	-70
-3	531	-515
-2	622	591
-1	287	270
0	228	231
1	428	433
2	120	125
3	714	-721
4	195	-205
5	367	389
6	311	-346
7	-40	14
K= 5, L= 4		
-8	-37	-17
-7	82	-81
-6	253	244
-5	-41	42
-4	449	-465
-3	135	129
-2	284	291
-1	95	99
0	215	209
1	208	217
2	463	-468
3	227	-246
4	480	476
5	75	80
6	-49	-56
7	-34	33
K= 5, L= 5		
-8	-34	35
-7	84	79
-6	58	81
-5	385	-373
-4	265	-280
-3	405	420
-2	248	-243
-1	134	-140
0	124	121
1	181	-180
2	158	208
3	208	221
4	223	232
5	103	-104
6	-38	31
K= 5, L= 6		
-8	52	-44
-7	-38	2
-6	146	-167
-5	237	-231
-4	449	467
-3	58	-58
-2	345	-356
-1	258	251
0	59	58
1	163	-168
2	155	147
3	87	75
4	201	-201
5	109	115
6	-30	30
K= 5, L= 7		
-7	-33	-33
-6	71	66
-5	253	281
-4	58	91
-3	335	-305
-2	217	210
-1	-46	-26
0	624	-616
1	316	306
2	-51	-14
3	267	-274
4	150	143
5	74	114
K= 5, L= 8		
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-5	108	123
-4	244	-270
-3	116	-127
-2	85	88
-1	232	-227
0	230	223
1	123	116
2	237	-219
3	-36	-21
K= 5, L= 9		
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-2	85	53
-1	-39	-44
0	269	213
1	115	-105
2	190	-205
K= 6, L= 0		
0	416	-304
1	831	-844
2	205	-205
3	302	376
4	-33	41
5	86	100
6	271	271
7	320	-315
8	-37	0
K= 6, L= 1		
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-7	116	106
-6	395	-395
-5	-38	-7
-4	70	79
-3	93	-46
-2	941	952
-1	242	244
0	955	-970
1	369	-357
2	927	899
3	-30	-16
4	273	-256
5	-40	39
6	351	-352
7	-50	-25
8	106	185
K= 6, L= 2		
-8	-38	-44
-7	334	-332
-6	134	-130
-5	299	309
-4	142	153
-3	460	454
-2	325	309
-1	905	-920
0	-27	-34
1	561	575
2	267	-252
3	110	94
4	211	-206
5	199	-204
6	-50	-37
7	160	161
8	65	84
K= 6, L= 3		
-8	139	-142
-7	120	-114
-6	352	331
-5	121	122
-4	216	-203
-3	177	157
-2	819	-878
-1	129	-138
0	766	789
1	71	57
2	224	211
3	66	57
4	89	-74
5	169	-182
6	150	176
7	-38	23
K= 6, L= 4		
-8	-35	11
-7	168	154
-6	-49	-41
-5	524	-522
-4	176	-188
-3	311	-319
-2	167	-163
-1	902	911
0	489	476
1	661	-718
2	261	254
3	160	184
4	168	-174
5	117	111
6	99	-101
7	-32	-33
K= 6, L= 5		
-8	123	147
-7	-43	-4
-6	169	-167
-5	112	-98
-4	118	115
-3	99	-107
-2	534	527
-1	290	288
0	1208	-1266
1	-37	-26
2	433	448
3	-45	35
4	126	131
5	-49	21
6	-36	-33
K= 6, L= 6		
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-6	-49	30
-5	152	149
-4	-47	-29
-3	90	81
-2	153	-152
-1	569	-577
0	129	-139
1	274	266
2	-47	47
3	183	177
4	251	252
5	247	-235
K= 6, L= 7		
-7	-31	7
-6	90	91
-5	-49	-29
-4	-52	60
-3	-50	-20
-2	148	-140
-1	195	-182
0	365	367
1	87	65
2	175	-187
3	132	125
4	223	-223
K= 6, L= 8		
-6	-31	19
-5	-37	19
-4	108	122
-3	-49	-52
-2	-51	-21
-1	312	303
0	-50	-43
1	432	-407
2	101	-100
3	105	115
K= 6, L= 9		
-4	54	-81
-3	-36	-28
-2	164	190
-1	-37	-30
0	234	-238
1	-33	-50
K= 7, L= 0		
1	-28	24
2	1317	-1362
3	150	-140
4	368	369
5	172	174
6	57	-88
7	-50	-21
8	-34	17
K= 7, L= 1		
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-7	-51	4
-6	111	123
-5	188	-196
-4	150	-161
-3	359	366
-2	125	136
-1	332	-346
0	140	114
1	365	-367
2	223	-219
3	634	639
4	-36	63
5	260	-272
6	-50	1
7	118	-115
8	54	53
K= 7, L= 2		
-8	-34	-8
-7	-50	-9
-6	378	-379
-5	177	-178
-4	329	334
-3	287	287
-2	536	-575
-1	86	-78
0	772	759
1	55	-77
2	655	715
3	-34	40
4	525	-544
5	128	-124
6	93	-91
7	106	99
K= 7, L= 3		
-8	-36	-8
-7	131	-130
-6	136	-118
-5	214	221
-4	155	155
-3	445	-447
-2	188	-192
-1	132	122
0	302	193
1	415	415
2	58	102
3	676	-644
4	293	-260
5	321	329
6	-49	63
7	63	67
K= 7, L= 4		
-8	-32	65
-7	-44	-31
-6	305	259
-5	69	78
-4	549	-555
-3	157	-202
-2	-34	-21
-1	-39	51
0	155	148
1	234	236
2	514	-535
3	108	-122
4	736	747
5	-52	-39
6	-35	-20
7	-30	-35
K= 7, L= 5		
-7	115	134
-6	-51	74
-5	436	-428
-4	184	-186
-3	230	244
-2	-38	38
-1	161	-163
0	109	112
1	76	-85
2	-43	42
3	203	200
4	-52	-24
5	-44	-48
6	-33	-44
K= 7, L= 6		
-7	-34	17
-6	192	-160
-5	-57	-71
-4	592	576
-3	144	135
-2	253	-242
-1	156	-190
0	150	-158
1	88	78
2	78	-77
3	106	107
4	158	-154
5	96	-46
K= 7, L= 7		
-6	-36	-12
-5	297	327
-4	110	121
-3	256	-265
-2	253	-235
-1	196	-185
0	-51	67
1	313	297
2	-50	75
3	312	-302
4	-33	-28
K= 7, L= 8		
-5	-34	55
-4	361	-341
-3	-44	-62
-2	238	247
-1	-48	7
0	391	375
1	-41	0
2	304	-284
3	-31	-5
K= 7, L= 9		
-4	-30	-3
-3	200	275
-2	-34	56
-1	-34	43
0	55	-63
1	112	-129
K= 8, L= 0		
0	402	-409
1	444	-464
2	135	-113
3	-34	-21
4	74	71
5	141	133
6	89	-88
7	167	-190
8	-31	-35
K= 8, L= 1		
-8	58	43
-7	68	-60
-6	424	-405
-5	-44	14
-4	114	105
-3	67	65
-2	844	844
-1	248	233
0	372	-380
1	381	-373
2	227	214
3	95	83
4	162	-183
5	127	128
6	302	-300
7	-39	25
K= 8, L= 2		
-8	-32	22
-7	266	-260
-6	-51	19
-5	204	209
-4	60	-61
-3	209	227
-2	58	46
-1	410	-413
0	499	-483
1	402	408
2	258	258
3	118	108
4	156	144
5	291	-290
6	-51	-28
7	118	115
K= 8, L= 3		
-8	-31	-37
-7	-43	1
-6	173	162
-5	134	-125
-4	306	-309
-3	-36	-35
-2	495	-493
-1	-33	28
0	467	620
1	142	158
2	245	265
3	741	-745
4	176	-176
5	80	63
6	169	148
7	-31	30
K= 8, L= 4		
-8	77	-101
-7	74	68
-6	-52	82
-5	150	-182
-4	-43	33
-3	285	-296
-2	134	120
-1	547	542
0	74	-75
1	254	-245
2	400	-417
3	-45	-39
4	210	202
5	212	156
6	-37	-38
K= 8, L= 5		
-7	104	123
-6	-47	-46
-5	-51	36
-4	-47	-8
-3	121	-115
-2	322	342
-1	65	83
0	763	-778
1	156	-168
2	-46	59
3	164	164
4	312	304
5	67	-44
6	-30	0
K= 8, L= 6		
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-6	-38	-48
-5	59	107
-4	108	-108
-3	-45	44
-2	272	274
-1	353	-345
0	82	-78
1	-48	43
2	136	132
3	232	225
4	167	-156
5	190	-203
K= 8, L= 7		
-6	-32	38
-5	-38	71
-4	54	110
-3	-51	62
-2	-52	-62
-1	-52	52
0	222	215
1	-51	-56
2	142	-133
3	55	-100
4	275	-297
K= 8, L= 8		
-5	-31	93
-4	85	-105
-3	114	-123
-2	-41	-23
-1	244	241
0	-40	14
1	190	-170
2	-33	-25
K= 8, L= 9		
-3	-30	-23
-2	178	228
-1	112	144
0	-30	-33
K= 9, L= 0		
1	77	-81
2	380	-384
3	176	169
4	133	134
5	54	96
6	-52	-25
7	92	-95
K= 9, L= 1		
-7	59	-54
-6	-52	-8
-5	168	-167
-4	256	-253
-3	303	295
-2	172	-186
-1	-32	13
0	213	203
1	244	-244
2	439	426
3	216	215
4	-43	54
5	-45	-55
6	134	-141
7	145	-143
K= 9, L= 2		
-7	81	-83
-6	-52	-40
-5	93	-83
-4	130	130
-3	60	-55
-2	228	-233
-1	140	142
0	-33	12
1	-34	45
2	463	471
3	125	-131
4	164	-177
5	-51	45
6	233	-227
7	141	145
K= 9, L= 3		
-7	50	83
-6	-53	7
-5	-45	28
-4	217	223
-3	217	-223
-2	348	-343
-1	-35	-56
0	266	-273
1	391	396
2	-39	-46
3	180	-175
4	165	156
5	-51	-17
6	227	229
K= 9, L= 4		
-7	-34	41
-6	113	111
-5	-51	3
-4	227	-234
-3	119	-141
-2	125	-124
-1	64	-60
0	222	227
1	-41	-10
2	157	-201
3	82	74
4	245	227
5	95	-92
6	55	50
K= 9, L= 5		
-7	-52	44
-6	109	-114
-5	151	-147
-4	206	200
-3	165	160
-2	186	183
-1	-44	1
0	-44	-41
1	330	-327
2	182	-190
3	243	256
4	165	-166
5	122	126
K= 9, L= 6		
-6	-35	-17
-5	132	143
-4	242	245
-3	56	53
-2	67	-74
-1	204	-187
0	368	-373
1	-51	51
2	292	262
3	-44	-40
4	-36	-2
K= 9, L= 7		
-5	59	67
-4	-40	5
-3	-47	29
-2	141	-145
-1	241	-229
0	340	331
1	241	230
2	-38	51
3	152	-157
K= 9, L= 8		
-4	-32	-5
-3	123	127
-2	-37	-47
-1	58	108
0	244	246
1	76	-65
2	207	-225
K= 10, L= 0		
0	260	231
1	252	-244
2	309	307
3	160	-165
4	179	-184
5	203	189
6	278	-226
7	-34	38
K= 10, L= 1		
-7	132	-136
-6	180	-166
-5	-50	-27
-4	211	231
-3	179	182
-2	72	-71
-1	255	-265
0	230	-232
1	281	286
2	-38	-5
3	-42	29
4	209	205
5	-52	-70
6	40	-82
7	70	79
K= 10, L= 2		
-7	76	-74
-6	207	197
-5	115	93
-4	251	-283
-3	136	-127
-2	404	-406
-1	119	-125
0	174	173
1	152	200
2	162	175
3	324	321
4	136	128
5	360	-344
6	76	75
K= 10, L= 3		
-7	117	132
-6	-43	4
-5	220	-216
-4	-47	48
-3	147	-136
-2	85	-92
-1	226	226
0	163	162
1	160	-162
2	-43	47
3	-47	31
4	342	-328
5	100	92
6	164	161
K= 10, L= 4		
-7	65	72
-6	88	99
-5	79	67
-4	-50	40
-3	137	-144
-2	265	267
-1	69	76
0	420	-427
1	-45	25
2	124	-127
3	129	-129
4	-50	66
5	155	203
K= 10, L= 5		
-6	-36	-40
-5	107	115
-4	102	-93
-3	-50	45
-2	119	110
-1	349	-334
0	-48	55
1	170	157
2	123	-121
3	-50	4
4	253	244
5	83	-85
K= 10, L= 6		
-6	65	60
-5	-38	15
-4	103	-115
-3	149	172
-2	109	124
-1	-57	-89
0	281	266
1	125	-122
2	-46	-73
3	266	192
4	221	-238
K= 10, L= 7		
-5	-31	30
-4	54	102
-3	-35	18
-2	182	-187
-1	155	181
0	-42	-63
1	196	-150
2	190	192
3	-30	-24
K= 10, L= 8		
-3	112	-206
-2	-33	5
-1	119	160
0	-32	0
1	76	101
K= 11, L= 0		
1	94	-103
2	-41	-94
3	293	290
4	281	274
5	213	-207
6	-34	17
7	-30	-5
K= 11, L= 1		
-7	59	-56
-6	174	-174
-5	232	-218
-4	253	229
-3	169	175
-2	459	-469
-1	-39	19
0	226	222
1	102	-105
2	367	381
3	-46	-6
4	194	-187
5	-50	-4
6	-37	30
K= 11, L= 2		
-7	41	-55
-6	56	105
-5	272	260
-4	164	55
-3	486	-488
-2	77	83
-1	188	192
0	384	-383
1	215	235
2	-44	-66
3	257	-256
4	-52	40
5	245	237
6	-34	13
K= 11, L= 3		
-7	90	120
-6	138	155
-5	58	56
-4	153	-181
-3	226	-218
-2	-45	31
-1	162	-165
0	-43	-70
1	303	300
2	257	-252
3	159	-150
4	357	383
5	101	-96
6	-30	0
K= 11, L= 4		
-6	-36	-46
-5	166	-155
-4	162	-145
-3	270	295
-2	258	294
-1	168	-160
0	307	251
1	222	-221
2	300	-286
3	220	290
4	164	-163
5	106	-91
K= 11, L= 5		
-6	164	-125
-5	-38	12
-4	351	411
-3	182	175
-2	199	-198
-1	-51	66
0	-51	-24
1	266	-275
2	-50	15
3	141	141
4	103	-105
K= 11, L= 6		
-5	152	191
-4	74	-79
-3	213	-215
-2	-48	10
-1	117	132
0	113	-103
1	68	56
2	308	300
3	202	-213
K= 11, L= 7		
-4	110	-150
-3	-35	-2
-2	162	182
-1	-38	-4
0	87	95
1	150	156
2	92	-102
K= 12, L= 0		
0	607	-639
1	345	-353
2	512	505
3	-48	68
4	-52	-9
5	157	143
6	168	-182
K= 12, L= 1		
-6	-36	19
-5	83	41
-4	100	101
-3	168	58
-2	225	-223
-1	520	-531
0	402	-400
1	539	539
2	166	157
3	-50	-40
4	272	280
5	211	-209
6	-32	-10
K= 12, L= 2		
-6	114	122
-5	-45	58
-4	105	-71
-3	79	-73
-2	161	-169
-1	214	-207
0	229	225
1	199	162
2	201	-182
3	-51	33
4	-49	-25
5	161	-158
6	107	119
K= 12, L= 3		
-6	54	70
-5	73	-64
-4	158	198
-3	74	-77
-2	-49	-67
-1	352	330
0	87	93
1	480	-477
2	252	-247
3	109	209
4	173	-189
5	160	158
K= 12, L= 4		
-6	82	-108
-5	-38	36
-4	-47	-14
-3	-52	-52
-2	333	333
-1	123	122
0	509	-574
1	175	-165
2	344	325
3	-44	-1
4	-36	45
K= 12, L= 5		
-5	-34	47
-4	67	-63
-3	155	155
-2	161	194
-1	302	-296
0	129	133
1	242	228
2	-42	37
3	142	-147
4	-30	3
K= 12, L= 6		
-4	-33	45
-3	175	206
-2	137	-142
-1	105	-103
0	212	201
1	-37	31
2	215	-222
K= 12, L= 7		
-3	91	-122
-2	176	-224
-1	212	252
0	-32	-2
1	127	-145
K= 13, L= 0		
1	-40	-63
2	-50	60
3	198	197
4	227	219
5	240	-253
6	49	-42
K= 13, L= 1		
-6	77	-92
-5	168	-151
-4	425	411
-3	210	212
-2	418	-350
-1	229	-224
0	161	157
1	-45	-50
2	-51	29
3	182	180
4	254	-217
5	67	-60
K= 13, L= 2		
-6	-30	15
-5	252	277
-4	250	285
-3	377	-367
-2	253	-242
-1	-50	11
0	231	-217
1	299	286
2	121	117
3	233	-220
4	109	-111
5	100	116
K= 13, L= 3		
-5	140	167
-4	390	-343
-3	190	-187
-2	216	208
-1	-51	13
0	364	355
1	88	103
2	325	-317
3	193	-185
4	141	163
K= 13, L= 4		
-5	109	-132
-4	-38	-60
-3	366	358
-2	242	236
-1	121	-111
0	-50	33
1	236	-218
2	145	-140
3	237	232
4	55	-70
K= 13, L= 5		
-4	167	203
-3	141	143
-2	318	-360
-1	-42	-40
0	-42	-9
1	58	-89
2	299	304
3	84	68
K= 13, L= 6		
-3	175	-223
-2	87	-115
-1	84	105
0	63	70
1	150	173
K= 14, L= 0		
0	662	-628
1	219	-209
2	195	177
3	141	157
4	69	85
5	-31	19
K= 14, L= 1		
-5	103	112
-4	115	-125
-3	-47	-37
-2	237	226
-1	260	-228
0	231	-241
1	253	236
2	-58	41
3	-46	25
4	80	99
5	159	-202
K= 14, L= 2		
-5	60	73
-4	-38	-16
-3	107	101
-2	78	98
-1	192	-191
0	271	249
1	86	79
2	171	-160
3	58	-47
4	247	-245
K= 14, L= 3		
-5	-30	18
-4	-36	-20
-3	-40	-30
-2	44	-40
-1	205	202
0	157	155
1	222	-216
2	230	-240
3	-34	23
4	51	65
K= 14, L= 4		
-4	89	-130
-3	-37	-55
-2	100	104
-1	227	244
0	127	-121
1	151	-165
2	220	223
3	-31	-29
K= 14, L= 5		
-3	96	134
-2	160	215
-1	79	-85
0	54	-110
1	68	60
2	-30	30
K= 14, L= 6		
-1	73	-107
K= 15, L= 0		
1	96	-89
2	77	-66
3	80	89
4	-32	-26
K= 15, L= 1		
-4	224	282
-3	-37	65
-2	98	-84
-1	151	-148
0	146	-161
1	-44	-30
2	-35	-13
3	131	145
4	-31	-61
K= 15, L= 2		
-4	63	54
-3	-37	-46
-2	148	-190
-1	-42	-49
0	95	87
1	131	131
2	125	142
3	103	-131
K= 15, L= 3		
-4	33	-38
-3	-34	49
-2	117	149
-1	-38	44
0	183	185
1	-37	-47
2	171	-169
3	46	-47
K= 15, L= 4		
-3	95	139
-2	-33	-35
-1	-34	92
0	69	-65
1	130	-143
2	-30	-10
K= 15, L= 5		
-1	-30	11
K= 16, L= 0		
0	70	-82
1	114	148
2	-34	-44
3	-31	8
K= 16, L= 1		
-3	-31	-9
-2	47	63
-1	-36	-34
0	128	142
1	-36	-33
2	-33	-24
3	-30	45
K= 16, L= 2		
-3	-30	47
-2	-33	11
-1	-35	40
0	71	80
1	110	-134
2	-31	-14
K= 16, L= 3		
-2	92	-82
-1	92	117
0	-32	-31
1	-31	24
K= 17, L= 0		
1	72	-109
K= 17, L= 1		
-1	82	76
0	-30	-3

ligand. Similarly small values of 83.4 and 83.7° were found in the $[ClNi(ATSC)_2]^+$ cation[4] and 89.1 and 90.5° in the Cl_2Zn . TSI complex.[6] Although the Cl1–Zn–Cl2 angle of 110.01(7)° is slightly larger than the tetrahedral value, the two Cl–Zn–S angles are much larger than the ideal value. The two S . . . Cl distances of 3.933 and 3.872 Å (both ±0.003 Å) are almost equal but larger than the sum of the van der Waals radii (3.65 Å). This observation suggests that the large Cl–Zn–S angles may be a consequence of the small S–Zn–N angle and not result from steric repulsion between Cl and S. A similar opening of the S–Zn–Cl angles to 115.6 and 121.8° was observed in the Cl_2Zn . TSI complex.[6] In the case of dichloro–(2,9–dimethyl–1,10–phenanthroline)zinc(II),[5] Cl_2Zn dmp, where dmp is the dimethyl–1,10–phenanthroline ligand, the Cl–Zn–Cl angle is large (120.3°) although the chelate angle, N–Zn–N of 81.5°, is small. These observations suggest that angular distortions may be a combination of steric and electronic effects.

Table IV. Bond angles (degree) in the molecule.* Estimated standard deviations are given in parentheses.

(a) Angles around zinc atom

Cl1-Zn-Cl2	= 111.01(7)	Cl1-Zn-N1	= 114.9(1)
Cl1-Zn-S	= 121.54(7)	Cl2-Zn-N1	= 103.7(1)
Cl2-Zn-S	= 116.43(7)	S-Zn-N1	= 85.2(1)

(b) Angles in the ATSC molecule

Zn-S-C1	= 96.0(2)	C3-C2-C4	= 118.8(5)
S-C1-N3	= 120.0(5)	Zn-N1-N2	= 112.0(3)
S-C1-N2	= 122.8(4)	Zn-N1-C2	= 129.5(4)
N2-Cl1-N3	= 117.2(5)	N2-N1-C2	= 118.2(5)
N1-C2-C3	= 124.8(5)	N1-N2-C1	= 121.3(5)
		N1-C2-C4	= 116.4(5)

* The angles involving hydrogen atoms were all chemically reasonable and are not listed.

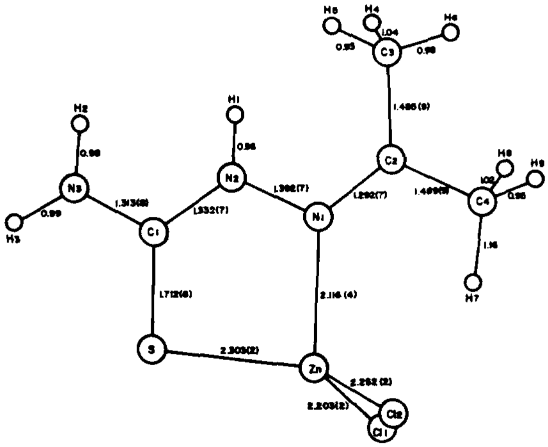

Figure 1. The atomic numbering and pertinent bond distances in the dichloro-(acetonethiosemicarbazone)zinc(II) complex. The estimated standard deviations are given in parentheses.

The two Zn–Cl distances of 2.203(2) and 2.252(2) Å are significantly different according to the criteria suggested by Cruickshank and Robertson[10] (t_o is 17.3). These Zn–Cl distances are at the lower half of the values summarized recently.[5] This compilation of the dimensions of $ZnCl_2Y_2$ complexes indicated that the Zn–Cl distances were a function of the donor properties of Y, an effect which is somewhat similar to the *trans* effect in square planar complexes. The difference in the two Zn–Cl distances may be related to the fact that Cl2 accepts two hydrogen bonding (see Table V and Figure 2). In compounds where no hydrogen bonds are possible,[5,11,12] the Zn–Cl distances tend to be shorter compared to those cases where hydrogen bonds may exist.[6,13] Although the hydrogen atoms were not located, the existence of hydrogen bonds involving the Cl atom was indicated by the short intramolecular distance of 3.23 Å in dichlorobis-(thiourea)zinc(II)[13] and several short intermolecular distances (N . . . Cl from 3.23 to 3.30 Å) in Cl_2Zn . TSI.[6] An accurate redetermination of these two compounds together with an extension to similar compounds will be required before any definitive conclusions can be made regarding the effect of hydrogen bonding on Zn–Cl distances.

The least-squares plane through S1, C1, N1, N2, and N3 has the equation $0.9365X+0.2321Y-0.2628Z=0.0767$ where X, Y, Z, are the cordinates (in Å) referred to the orthogonal axes a, b, c*. The displacements (in Å) from the plane are S1 of +0.000, C1 of –0.001, N1 of +0.000, N2 of +0.001 and N3 of 0.000, indicating the planarity of this portion of the ligand. However, the zinc atom is displaced by +0.433 Å from the plane of the ligand. This displacement from the plane is one of the largest observed to date for $ZnCl_2$ adducts with chelating ligands. Further distortions from mirror symmetry are exhibited by the $ZnCl_2$ group which is at an angle of 82.5° to the above plane. Similar distortions were observed in dichloro–(1,10–phenanthroline)zinc(II)[11] where the zinc ion is displaced by 0.13 Å from the plane of the 1,10–phenanthroline and the $ZnCl_2$ plane makes an angle of 79.0° with the ligand. However, in $ZnCl_2$. dmp the molecule has approximately C_{2v} symmetry.[5] Furthermore, in $ZnCl_2$. TSI[6] the zinc is coplanar with the TSI ligand which is very closely related to ATSC. Apparently the planarity of the Zn atom with chelating ligands in $ZnCl_2$ adducts is highly variable and the reasons for deviations from planarity are not well understood.

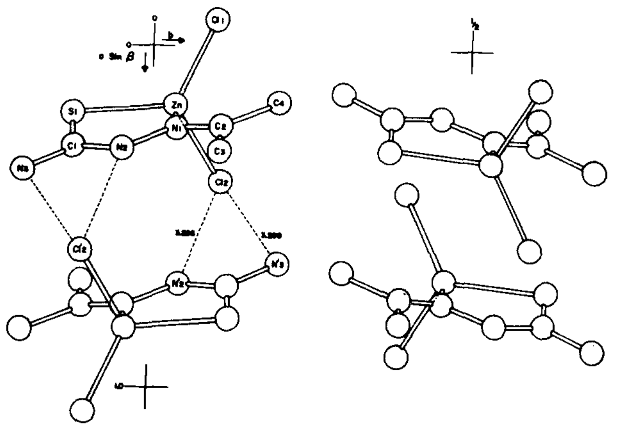

Figure 2. A view down c illustrating the molecular packing. The hydrogen bonds involving Cl2 are shown as broken lines together with the N. . . Cl2 distance.

The Zn–S distances reported in the literature for four coordinated zinc compounds range from Zn–S of 2.29 Å in Cl_2Zn . TSI[6] to 2.409 Å in bis(O,O–di-isopropylphosphorodithioate)zinc(II),[14] with our value of 2.303(2) Å near the low end of the range. Unfortunately not enough examples of compounds containing Zn–S bonds have been studied to permit a correlation of distance with ligand.

The molecular dimensions of the ATSC ligand are in excellent agreement with the values found in the ATSC ligand in the $Ni(ATSC)_2Cl^+$ cation.[4] There are small changes in bond distances in the complexed

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(10) D.W.J. Cruickshank and A.P. Robertson, *Acta Cryst.*, *6*, 698 (1953).

(11) C.W. Reiman, S. Block and A. Perloff, *Inorg. Chem.*, *5*, 1188 (1966).

(12) Y.A. Sokolova, L.O. Atovmyan, and M.A. Porai-Koshito, *J. Struct. Chem.*, *7*, 794 (1966).

(13) N.R. Kunchur and M.R. Truter, *J. Chem. Soc.*, 3478 (1958).

(14) S.L. Lawton and G.T. Kokotarlo, *Inorg. Chem.*, *8*, 2410 (1969).

Table V. Hydrogen Bonds.

Bond D—H . . . A *	Position of A	D-H(Å)	H-A(Å)	D - - - A(Å)	D-H - - - A angle(°)
N2-H1 . . . Cl2	1-x,-y,1-z	0.96	2.46	3.296(5)	145
N3-H2 . . . Cl2	1-x,-y,1-z	0.98	2.39	3.299(6)	155

* Donor-hydrogen . . . Aceptor. D-H at x,y,z.

versus the uncomplexed ATSC ligand.[15] The largest change occurs in the C–S bond which increases from 1.690(5) Å in ATSC[15] to 1.712(6) Å in Cl_2Zn ATSC and 1.719 Å in $Ni(ATSC)_2Cl^+$ cation.[4] The difference between the C–S bond in uncomplexed ATSC and the ATSC ligand in the Cl_2Zn ATSC complex is significant ($t_o = 2.8$) as would be expected. A similar increase in the C–S bond length with chelation was observed in the nickel complexes of thiosemicarbazones[3,4] and also thiourea.[16]

The packing of the molecules in the unit cell as viewed along *c* is shown in Figure 2. The two hydrogen bonds involving the Cl2 are shown as dotted lines. The dimensions of these two hydrogen-bonds are given in Table V. The hydrogen bonds are between two molecules related by a center of symmetry resulting in dimer-like units are packed together with only the usual van der Waals forces existing between these units. There is only one contact less than 3.5 Å between the non-hydrogen atoms which is a Cl1— distance of 3.450 Å that is slightly shorter than the sum of the van der Waals radii of 3.65 Å.

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(15) W. Carter and G.J. Palenik, unpublished results.

(16) M. Nardelli, G. Gasparri, G.G. Battistini, and P. Domiano, *Acta Cryst.*, *20*, 349 (1966).