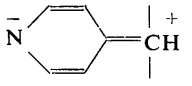
1·61 Å. Even allowing for a fairly large error in the bond length, the value is still larger than is usually observed for single C–C bonds. The strains introduced by the bonding to form the cage, especially in closing the C(7)–C(7′) bond, are probably relieved by this somewhat long bond.

The distances and angles in the pyridine ring are also somewhat unusual. The bond formed by C(2)–C(3) is only 1·34 Å as compared with 1·41 Å for C(3)–C(4). Also, C(4)–C(5) at 1·47 Å is considerably shorter than a single-bond value. The arrangements of the bond lengths resemble those from a quinoid type structure:



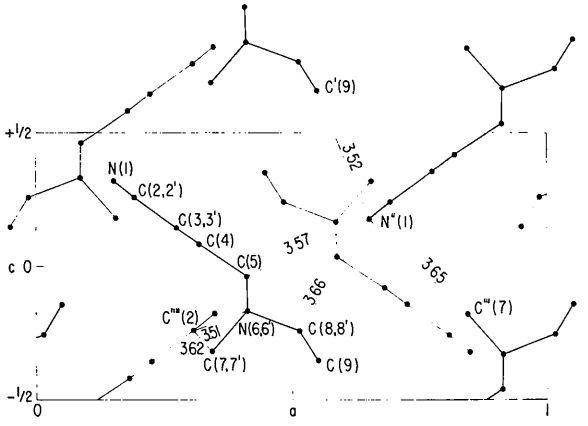


Fig. 4. The contents of a unit cell viewed along the *b* axis. All the intermolecular distances less than 3·8 Å are indicated in the figure.

A similar situation has been found for 4-nitropyridine *N*-oxide (Eichhorn, 1956) with bond lengths and angles in the pyridine ring almost identical with those found in the present investigation.

Fig. 4 illustrates the contents of the unit cell and the nearest approaches between molecules. N(1) of the pyridine ring is surrounded by six atoms of neighboring molecules at distances of 3·52–3·66 Å. The only other near approach is in the **b** direction between atoms C(2) of one molecule and N(6) and C(7) of another at 3·51 and 3·62 Å.

The authors are grateful to Mr Stephen Brenner for preparing and revising programs for data reduction and phase determination, and to Dr Donald Mitchell for performing the computations.

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The Crystal Structure of Zinc Dimethyldithiocarbamate

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(*Received* 20 *January* 1966)

The crystal structure of zinc dimethyldithiocarbamate, $Zn[S_2CN(CH_3)_2]_2$, has been determined from three-dimensional Weissenberg data and refined by anisotropic least-squares methods. The crystals are monoclinic, space group $C2/c$, with $a = 8{\cdot}455 \pm 0{\cdot}003$, $b = 15{\cdot}747 \pm 0{\cdot}005$, $c = 18{\cdot}345 \pm 0{\cdot}009$ Å, $\beta = 104{\cdot}76 \pm 0{\cdot}04°$. The cell contains the content of eight monomeric molecules.

The most interesting finding is the binuclear nature of molecules of the compound in the crystal. These binuclear molecules, of formula $Zn_2[S_2CN(CH_3)_2]_4$, lie on twofold axes. The coordination of sulfur about each zinc atom is distorted tetrahedral, with the average Zn–S distance 2·362 Å. The Zn···Zn distance in the molecule is 3·973 Å. The dimethyldithiocarbamate groups deviate slightly from planarity, and are of two types. Each group of the first type is chelated directly to its own zinc atom of a tetrahedron, then two of the second type act as bridging ligands between the two zinc–sulfur tetrahedra in the molecule. The molecule appears not to vibrate or librate as a rigid body. Intermolecular distances are completely normal.

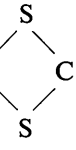
Introduction

The dithiocarbamates find wide application in inorganic analysis, in rubber chemistry and technology, and in agriculture as fungicides. Nevertheless, despite our increasing knowledge of dithiocarbamate chemistry, their mode of action as biocides has not yet been

explained (Thorn & Ludwig, 1962). In this respect, structural information on them could be extremely useful, and laboratories in several countries have lately made the metal dialkyldithiocarbamates the object of study. Aside from the biological implications, interest centers in the coordination geometry about the metal atom and in the structure and planarity of the dithiocarbamate group.

Alderman, Owston & Rowe (1962) reported on the structure of $Co(NO)[S_2CN(CH_3)_2]_2$, in which the coordination polygon around the Co atom is a rectangular based pyramid with the NO group at the apex and the four S atoms at the corners of the base. The $S_2CN(CH_3)_2$ ligands are planar, and the Co atom is coplanar with each dithiocarbamate group. Most remarkable, too, the NO group is π-bonded about its middle to the Co atom. Hesse (1963) found discrete $[CuS_2CN(C_2H_5)_2]_4$ molecules in the cuprous diethyl compound. The four Cu(I) atoms are arranged in a tetrahedral configuration at the center of the molecule. The Cu(II), Ni(II), and Zn(II) diethyldithiocarbamates were reported on briefly by Bonamico, Vaciago & Zambonelli (1963) at the Sixth Congress of the International Union of Crystallography, Rome. More recently details of these studies have been presented. The Ni compound has square-planar coordination of the S atoms about the Ni atom (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965; hereafter designated BDMVZ). In the Cu(II) compound the coordination is closely related to a tetragonal pyramid, the Cu atom having a coordination number of 5 with a long bond to a second molecule related by a center of symmetry (Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965). Finally, in the Zn compound, although the coordination about each Zn atom is distorted tetrahedral, two molecules are joined to form a binuclear complex. In this complex each of the two Zn atoms has one dithiocarbamate group wholly within its coordination sphere and another that links it with the coordination sphere of the neighboring Zn atom (Bonamico, Mazzone, Vaciago & Zambonelli, 1965; hereafter designated BMVZ).

Before the Rome Congress, 1963, the author had begun studies of zinc dimethyldithiocarbamate (ZTC)*, $Zn[S_2CN(CH_3)_2]_2$, for the purpose of investigating the coordination about the Zn atom, the structure of the thiocarbamate groups, and the geometry of the four-membered



rings anticipated to be present†.

This communication presents the results of a detailed investigation of the molecular and crystal structure of ZTC.

Crystal data

ZTC is essentially insoluble in water, and only very sparingly soluble in common organic solvents. The crystals used in this study were grown by slow cooling of hot saturated solutions of ZTC in chloroform.

Single-crystal diffractometer measurements of 21 moderately high-angle reflections using Cu $K\alpha$ (1·5418 Å) radiation and a line focus provided the data for a least-squares determination of the cell constants and e.s.d.'s by an IBM 7090 program adapted from the University of Washington Param refinement program. These results and other crystal data on ZTC are summarized below:

$a = 8{\cdot}455 \pm 0{\cdot}003$, $b = 15{\cdot}747 \pm 0{\cdot}005$,
$c = 18{\cdot}345 \pm 0{\cdot}009$ Å, $\beta = 104{\cdot}76 \pm 0{\cdot}04°$.

$Z = 8$, M.W. 305·80,
$D_x = 1{\cdot}72$ g.cm^{-3}, $D_m = 1{\cdot}66$ g.cm^{-3}.

Monoclinic, space group $C2/c$; $F(000) = 1248$ (corrected for dispersion = 1244).

Determination of the structure

The structure has been determined from visually estimated, a- and c-axis, Cu $K\alpha$ Weissenberg intensity data. Crystals used for the intensity measurements were of such shape and dimensions, and were so oriented, as usually to keep absorption paths within them $\lesssim 0{\cdot}5$ mm. No corrections were made for absorption or extinction. The 1625 measured independent reflection intensities were corrected as usual, and put on an approximate absolute basis with a Wilson plot. It was estimated that ~2800 independent reflections were available in the Cu $K\alpha$ sphere. Since observed reflections of all expected types extend out to the limit of the sphere of reflection, the additional 1175 unobserved reflections were considered to be too weak to measure. The corrected reflection intensities were reduced to F's and to normalized structure factors, E's.

ZTC's space group, $C2/c$, should permit phase determination by the symbolic addition procedure (Karle & Karle, 1963) based on the Σ_2 relation (Sayre, 1952; Hauptman & Karle, 1953). The first attack on the structure was by this procedure using the IBM 1620 computer program of Beurskens (1963) (see also Kim, 1964). The method did not yield a unique set of signs, but ended up with four solutions to be tested, a result

* Zinc dimethyldithiocarbamate is marketed by the Monsanto Chemical Co., St. Louis, Missouri, U.S.A., under the trade name 'Methasan'. The author gratefully acknowledges Monsanto's gift of a generous sample for use in this study.

† At the Rome Congress Dr Marjorie Harding disclosed that some preliminary studies of ZTC had been made at the University of Edinburgh. At this time Dr Harding decided to discontinue her work on ZTC, in favor of other investigations of greater immediate interest, and graciously encouraged the author to continue his study of the compound.

that may have been due to computer storage limitations which prevented the use of all of the high E-value data. To bring the data into the range of the program a selection was made which enabled most of the E's >2 to be used, but did eliminate many in the range, $1 \lesssim E \lesssim 2$. Only the signs from set II of the four solutions yielded a three-dimensional Fourier synthesis that appeared to place zinc and sulfur atoms in reasonable positions. The arrangement was a rather distorted tetrahedral grouping of the sulfur atoms about the zinc, with the Zn–S distances near enough to expected values to give some confidence in the result. On the negative side, the arrangement appeared to place the ZnS_4 tetrahedra too close to each other, and the many smaller peaks made no sense as carbon and nitrogen atom positions.

A three-dimensional sharpened Patterson synthesis seemed to confirm the zinc and sulfur atom positions obtained from sign set II. Because of the complexity of the Patterson diagrams it was not possible, of course, to determine any carbon or nitrogen atom positions directly therefrom. At this point approximately 500 of the strongest reflections gave an $R=0{\cdot}275$ based on the zinc and sulfur atoms only. A least-squares refinement of the zinc and sulfur parameters reduced the R to 0·201. A three-dimensional Fourier synthesis based on the refined zinc and sulfur positions still failed to provide interpretable positions for the carbon and nitrogen atoms.

The author's preconceived model for the ZTC molecule was a linear one, $(H_3C)_2NCS_2ZnS_2CN(CH_3)_2$, with the sulfur atoms tetrahedrally arranged around the zinc atom and with the planes of the thiocarbamate groups at right angles to each other. The cell dimensions and the close approach of two ZnS_4 tetrahedra, however, seemed to rule out this model. A slight resemblance of the b-axis projection of the pair of ZnS_4 tetrahedra to that in the binuclear molecule reported by Bonamico, Vaciago & Zambonelli (1963) for the zinc diethyl compound was now recognized and led to the solution of the structure. Although the two tetrahedra in the diethyl compound are related by a center of symmetry, and those in ZTC are related by a two-fold axis, ultimately a binuclear structure was proved to be present in ZTC also. It was necessary to locate the carbon and nitrogen atoms of the thiocarbamate groups, atom by atom, by postulating their positions assuming a planar thiocarbamate group and C–S, N=C and C–N distances as previously observed.

Finally, a complete set of parameters was obtained for all atoms (except the hydrogen atoms) which, with isotropic temperature factors, gave an R of 0·130 for the 500 strongest reflections. When correction for anomalous dispersion (imaginary component ignored) was introduced for the zinc and sulfur atoms (*International Tables for X-ray Crystallography*, 1962, p.214), and all 1625 reflections were included, R increased to 0·192. On introducing anisotropic temperature factors, least-squares refinement of these parameters resulted in an $R=0{\cdot}121$ and a weighted $R'=0{\cdot}153$, based on observed reflections only. The value of the quantity $[\Sigma w(\Delta F^2)^2/(n-p)]^{\frac{1}{2}}$ – the standard deviation of an observation of unit weight – is 1·7. Defining Δ as the change in a parameter in the last least-squares cycle, and σ as the e.s.d. of the parameter for that cycle, refinement was terminated when the maximum Δ/σ for any positional parameter was $<0{\cdot}25$ and for any temperature β_{ij} was $<0{\cdot}50$. For the positional parameters the average Δ/σ was 0·064 and the maximum 0·227; for the β_{ij}'s the average was 0·088 and the maximum 0·416. Since F_c for $\bar{1}11$, $\bar{2}04$, and $\bar{4}04$ is always calculated much larger than F_o, it was judged that these strong reflections suffer from extinction. On excluding them in the calculation of R a final value of 0·118 was obtained. In the least-squares calculations the function minimized was $\Sigma w(F_o-F_c)^2$. Cruickshank's (1961) weighting scheme was used with Shiono's (1965) IBM 7090 modification of the Busing, Martin & Levy (1962) full-matrix program. Three-dimensional Fourier and difference Fourier, syntheses were computed with an IBM 7090 program prepared by Shiono (1965) and based on a program written by Dr A. Zalkin, University of California, Berkeley.

Since methyl hydrogen atoms have been successfully located in some crystals (Sutor, 1963; Palenik, 1964; Hall & Maslen, 1965), it was attempted for ZTC. A three-dimensional difference Fourier synthesis, subtracting out the 13 heavy atoms of the asymmetric unit, was prepared. The methyl hydrogen atoms were then sought, assuming they must lie at positions 120° apart on the periphery of a disc of radius 1·03 Å perpendicular to the N–C bond extension and whose center is about 0·37 Å from the carbon atom. This picture assumes an N–C–H bond angle of about 110° and a C–H distance of about 1·09 Å. It was possible to pick out likely hydrogen atom positions on or very close to 12 peaks in the difference synthesis, although these 12 peaks were not necessarily the strongest peaks in the synthesis. However, when the best possible set of hydrogen atom parameters was achieved by this procedure, their inclusion (with a suitable temperature factor) in calculating the structure factors failed to make any significant change in the R value. It was concluded that the hydrogen atoms could not be located from the data available.

The observed and calculated structure factors are listed in Table 1. The fractional atomic coordinates, the atomic anisotropic thermal parameters from the anisotropic least-squares refinement, and the estimated standard deviations of each are presented in Table 2. The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen, and zinc, those of Tomiie & Stam (1958) for sulfur, and those of McWeeny (1951) for hydrogen. The estimated standard deviations of the parameters were calculated from the sum of the residuals and the diagonal terms of the inverse matrix of the least-squares normal equations.

Table 1. *Observed and calculated structure factors*

The data are separated into groups having common h and k values.
The three columns of each group list values of l, F_o and F_c in that order.

h = 0, k = 0

2	49	-41
6	86	71
8	371	376
10	155	-129
12	87	68
14	80	67
16	93	-84
18	82	-90
20	53	55
22	33	31

h = 0, k = 2

0	40	-42
1	175	192
2	259	258
3	119	111
4	20	17
5	28	-19
6	112	-149
7	17	7
8	54	-46
9	241	244
10	207	188
11	40	36
14	137	-125
15	84	78
17	123	118

h = 0, k = 4

0	100	-90
2	51	44
3	19	8
4	186	-192
5	32	26
6	90	-82
7	64	58
8	188	-166
9	20	-16
10	117	95
12	29	29
13	30	29
14	83	-85
16	143	-135
17	44	-45
18	60	62
20	53	51
22	22	-30

h = 0, k = 6

0	168	150
1	234	-234
2	139	126
3	24	-18
4	65	-58
5	127	103
6	69	-55
7	33	33
8	88	77
9	198	-183
10	116	101
11	52	46
12	21	-18
13	44	38
14	32	-28
15	91	-85
17	53	-54

h = 0, k = 8

0	407	425
1	184	176
2	19	-7
3	61	56
4	55	-57
5	69	-62
6	26	22
7	27	19
8	206	193
9	168	158
10	68	-61
12	63	62
14	32	27
15	83	80
16	43	-40
17	40	47
18	64	-58
20	62	59

h = 0, k = 10

0	112	-103
1	87	83
4	32	27
5	81	72
6	161	-154
7	21	-10
8	112	-98
9	118	115
10	127	119
11	52	48
12	23	19
13	32	31
14	101	-109
15	30	33
16	39	-44
17	82	73
18	54	52

h = 0, k = 12

0	88	-80
1	84	-80
2	33	25
3	29	22
4	131	-132
6	51	-46
7	69	71
8	77	-75
9	73	-71
10	59	62
13	29	31
14	40	-32
16	40	-40
17	65	-67
18	26	26

h = 0, k = 14

0	141	137
1	66	-60
3	33	-9
4	64	-68
5	45	48
8	77	79
9	61	-63
10	29	24
11	38	38
14	23	27
15	42	-40

h = 0, k = 16

0	96	92
1	85	87
2	29	-26
3	38	42
5	60	-67
6	39	-45
8	45	47
9	91	99
11	24	-26
12	45	40

h = 0, k = 18

0	68	-76
3	37	-45
4	25	-22
5	64	63
6	61	-69
7	22	-27
8	57	-63
10	46	51

h = 0, k = 20

1	36	-47
4	42	-55

h = 1, k = 1

0	185	179
2	60	50
3	105	95
4	151	-152
5	210	-214
6	62	-63
7	65	-61
8	87	82
9	44	34
10	50	40
11	14	-3
12	38	-27
13	140	-134
14	77	72
15	47	38
20	23	21
21	104	-31
22	88	91

h = -1, k = 1

1	218	259
2	81	-132
3	37	44
4	82	-107
5	88	-101
6	31	33
7	27	24
8	83	79
9	271	222
10	97	-84
11	94	-108
13	37	-22
14	40	-27
15	77	64
16	51	-42
17	63	57
18	77	-70
19	88	-94
20	36	38
21	33	22
22	24	-23
23	24	25

h = 1, k = 3

0	113	-112
1	55	-56
3	72	70
4	95	91
5	60	-53
6	67	-56
7	98	-87
8	196	-166
9	33	-34
10	31	31
11	68	65
12	105	104
13	110	-107
14	93	-101
15	29	-17
16	78	-81
19	35	27
20	71	50
21	69	-67

h = -1, k = 3

1	86	86
2	160	160
3	48	-42
4	47	45
5	25	20
6	95	-89
7	37	27
8	24	18
9	68	63
10	222	218
11	40	-37
12	40	13
13	54	50
14	57	-56
17	42	40
18	112	107
19	27	-28

h = 1, k = 5

1	82	78
3	123	-110
4	74	60
5	134	117
6	102	-109
7	153	130
8	22	-16
10	21	20
11	107	-103
12	75	81
13	146	148
14	78	-76
17	40	-34
19	33	-30
20	110	31
21	103	92

h = -1, k = 5

1	187	-202
2	62	57
3	25	19
4	46	-45
5	14	12
6	27	-29
7	60	-58
8	22	-16
9	151	-127
10	160	150
11	95	85
12	42	-37
13	28	-19
14	29	-19
16	26	-25
17	51	-50
18	75	68
19	59	67

h = 1, k = 7

0	155	181
1	86	-84
2	117	101
4	219	-208
5	65	52
6	24	15
7	23	-20
8	98	77
9	49	-45
10	74	70
11	54	37
12	58	-59
13	33	21
14	115	116
15	41	-45
17	26	26
18	24	13
19	19	17
20	12	11

h = -1, k = 7

1	64	-68
2	152	-145
3	30	-23
4	153	-144
5	69	60
6	25	26
8	102	99
9	71	-67
10	159	-172
11	49	47
12	20	22
14	29	-27
15	29	-28
16	42	-37
18	103	-105
19	42	41
20	57	64
21	30	-22

h = 1, k = 9

0	41	32
1	63	57
2	27	22
3	38	33
4	13	-4
5	185	-159
6	94	-87
7	106	-103
8	20	-14
9	57	55
10	41	31
11	36	-35
13	103	-115
15	28	21
16	26	-27

h = -1, k = 9

1	204	217
2	30	-10
3	64	56
4	12	-1
5	108	-98
6	38	-39
7	61	56
8	23	25
9	175	171
10	67	65
11	82	-70
13	30	-33
14	51	-50
15	65	79
17	37	45
18	24	22
19	82	-87

h = 1, k = 11

0	34	-24
1	40	-39
2	36	-24
3	18	16
4	55	52
5	32	25
6	44	-41
7	29	26
8	120	-107
9	60	-64
11	40	40
12	77	86
13	20	-26
14	78	-92
16	82	-86

h = -1, k = 11

1	66	-65
2	107	101
3	58	-54
5	72	63
6	38	-32
7	34	-27
8	30	22
9	33	-28
10	150	157
13	65	73
15	49	-43
18	76	87

h = 1, k = 13

0	38	31
1	59	60
2	72	67
3	45	-45
4	30	-29
5	86	81
6	68	-67
7	63	66
8	43	38
9	23	14
10	48	55
11	47	-60
12	26	-5
13	78	95
15	12	-7
16	28	26

h = -1, k = 13

1	120	-118
2	34	-29
4	49	-44
7	30	-31
9	82	-82
10	30	26
11	55	60
12	19	-24
13	26	-23
14	25	-21
16	20	-17
17	29	-27

h = 1, k = 15

0	106	113
1	35	-30
2	29	22
3	29	26
4	72	-83
6	35	17
7	51	-57
8	38	42
11	20	22
13	32	-28
14	58	64

h = -1, k = 15

1	46	40
2	64	-65
4	88	-99
6	29	9
7	29	29
8	46	46
9	27	14
10	84	-91

h = 1, k = 17

0	28	-29
2	22	21
4	29	31
5	60	-72
6	46	-57
7	19	-22
8	43	-51
10	29	32

h = -1, k = 17

1	66	75
2	26	22
3	22	17
4	32	39
6	44	-55
7	71	69
10	82	85
11	36	-43
12	26	25

h = 1, k = 19

0	23	23
2	11	-8
5	52	56
6	14	-17
7	24	33

h = -1, k = 19

1	55	-64
2	32	34
3	29	-27
4	32	-36
5	17	17
6	23	7
7	25	-21
8	21	22

h = 2, k = 0

0	151	-140
2	159	147
4	381	-415
6	153	-81
8	145	-117
10	45	38
12	29	-26
14	31	26
16	43	-36

h = -2, k = 0

2	192	-197
4	418	-624
6	177	186
8	64	-53
10	85	-98
12	57	-51
14	112	98
16	82	-78
20	139	142

h = 2, k = 2

0	16	-15
1	112	-117
2	184	147
3	234	211
4	43	38
5	112	-99
6	200	-187
7	163	-149
9	49	-52
10	116	109
11	101	91
12	36	37
13	167	-161
14	44	46
15	70	-69
21	68	-84

h = -2, k = 2

1	88	81
2	218	-231
3	144	-161
4	12	12
5	184	-212
6	144	-146
7	55	67
8	28	21
9	63	-57
10	99	91
11	192	-173
13	73	-66
14	146	-125
16	31	27
17	70	-58
18	97	86
19	93	-89

h = 2, k = 4

0	226	224
1	43	43
2	155	-124
3	108	-118
4	281	257
5	54	-39
6	78	67
7	46	36
8	75	-58
9	17	-15
10	29	-25
11	87	-81
12	319	313
13	53	47
15	31	19
16	79	-82
20	88	98

h = -2, k = 4

1	32	-31
2	135	133
3	81	83
4	91	-93
5	17	10
6	145	-147
7	63	-57
8	203	215
9	13	-8
10	121	99
11	23	18
12	96	-89
14	67	-58
15	31	-18
16	58	39
18	30	28

h = 2, k = 6

1	13	7
2	224	179
3	220	-179
4	88	-77
5	89	72
6	228	-200
7	23	11
8	26	18
10	88	81
11	50	-45
12	58	-48
13	83	76
15	43	39
18	41	-52
20	26	-26

h = -2, k = 6

1	13	-10
2	253	-225
3	29	16
4	66	-56
5	201	209
6	19	15
7	88	-81
8	22	-21
9	28	-21
11	112	107
12	20	20
13	60	57
14	75	-64
15	54	-54
17	22	20
18	41	40
19	86	88
20	43	40
21	26	-30

h = 2, k = 8

0	27	-13
1	33	-26
2	115	102
3	70	59
4	173	-198
5	94	-83
6	51	-49
7	56	-50
8	98	-94
9	33	-28
10	40	36
12	49	-41
13	44	-43
14	33	32
15	35	-34
16	60	-61
18	21	-21

h = -2, k = 8

1	65	54
2	126	-111
3	29	14
4	202	-238
5	149	-141
6	96	90
7	29	26
9	19	13
10	37	-42
11	99	-100
12	43	-30
13	69	-72
14	44	40
15	38	36
16	52	-50
17	29	-29
19	80	-79
20	83	83

h = 2, k = 10

0	17	15
1	126	-115
2	63	58
3	133	116
4	117	104
5	72	-61
6	28	-18
7	96	-93
8	39	-36
9	45	-48
10	42	41
11	54	53
12	118	112
13	114	-112
15	36	-41
16	33	-36
17	24	23
18	25	-20

h = -2, k = 10

2	71	68
3	68	-62
4	16	14
5	99	-89
6	68	-59
7	49	43
8	62	58
9	103	-95
10	128	130
11	79	-76
12	22	-21
13	31	-27
14	97	-94
15	29	-25
16	35	33
17	52	-51
18	58	59
19	36	-35
20	23	-24

h = 2, k = 12

0	139	134
1	87	86
2	19	-7
3	160	-157
4	119	122
5	20	-15
6	69	65
7	31	-12
9	84	-92
12	125	123
13	64	69
15	57	54
16	47	-51

h = -2, k = 12

1	19	-7
2	19	19
3	66	58
5	78	75
6	53	-47
7	101	-99
8	141	133
9	35	32
10	41	40
11	41	35
12	30	-31
14	35	-35
15	26	-21
17	15	24
19	21	22

h = 2, k = 14

0	25	24
1	36	-32
2	111	114
3	40	-31
4	79	-75
5	52	46
6	97	-108
7	43	-44
9	28	14
10	29	25
12	51	-56
13	35	36
14	29	-26

h = -2, k = 14

2	104	-99
4	64	-53
5	57	54
6	63	67
9	29	-28
10	29	-24
11	38	40
13	36	24
16	38	-40

h = 2, k = 16

0	33	3
2	57	60
3	51	58
4	43	-47
5	44	-46
8	58	-55
10	15	10
11	25	26

h = -2, k = 16

1	37	45
4	62	-65
5	82	-78
6	30	25
9	27	26
10	30	32
11	66	-70
12	25	-21
13	45	-38
14	25	-17

h = 2, k = 18

0	43	44
1	47	-49
3	38	41
4	69	73
8	24	-29

h = -2, k = 18

1	37	-41
2	39	44
4	23	20
6	27	-28
7	22	25
8	56	59
9	48	-54
10	45	61

h = 3, k = 1

1	16	-17
2	218	213
3	108	102
5	92	88
6	96	-88
7	14	-16
9	38	35
10	46	41
11	65	62
12	27	-22
13	61	63
14	47	-48
15	27	-28
18	56	-68
19	31	29
20	27	-37

h = -3, k = 1

2	68	-67
3	60	-56
4	16	-20
5	97	-112
6	126	155
7	100	92
8	44	-39
9	41	-41
10	31	25
11	34	-30
12	27	18
13	54	-42
14	36	28
15	109	90
16	39	-44
17	39	-40
18	72	67
20	34	40
21	22	18
23	37	39

h = 3, k = 3

0	92	77
1	102	-87
2	132	-143
3	134	129
4	68	72
5	97	82
6	59	49
7	88	-78
8	81	-76
9	54	54
10	58	-56
11	96	87
12	105	100
14	70	69
15	46	48
16	57	-86
17	73	84
20	26	35

h = -3, k = 3

1	27	23
3	102	-114
4	81	-88
5	38	-39
6	140	-169
7	108	116
8	125	130
9	72	-77
11	47	-42
12	118	-118
13	30	25
14	101	-98
15	47	41
16	67	64
17	73	-69
18	19	-21
19	26	23
20	29	-29

h = 3, k = 5

1	114	102
2	34	27
3	156	-174
5	154	-129
7	143	125
8	90	-81
9	64	-57
10	20	9
11	126	-121
12	33	29
14	38	32
15	68	75
16	34	-49
17	84	-103

h = -3, k = 5

1	31	-26
2	26	-13
3	196	192
4	40	-39
5	78	73
6	56	-57
7	158	-169
8	81	84
9	85	96
10	25	-16
11	76	69
12	25	-31
13	36	-34
14	71	-80
15	86	-89
16	47	46
17	79	78
19	35	-28
21	34	-35
22	16	-23

h = 3, k = 7

0	49	40
1	20	8
2	201	168
4	26	23
5	36	36
6	150	-135
7	49	-39
8	23	26
10	20	23
11	19	18
13	33	-28
14	68	-68
18	43	-55

h = -3, k = 7

1	37	35
2	111	-101
3	60	-57
5	45	45
6	185	174
8	38	-27
10	40	31
11	19	-19
12	26	29
13	33	36
14	72	69
15	27	-27
16	61	-67
18	66	71
20	43	44
22	12	8

h = 3, k = 9

0	28	-22
1	37	-33
2	113	97
3	163	135
5	76	63
6	19	-12
7	19	20
8	21	-19
9	30	22
10	30	38
11	81	84

Table 1 (*cont.*)

13	51	58
14	24	27
15	31	-33
17	27	34

h = -3, k = 9

1	40	-36
2	16	-13
3	54	-43
4	45	-44
5	105	-98
6	34	27
7	80	78
9	36	-32
10	36	37
11	44	-39
12	33	-33
13	19	-22
14	39	-37
15	71	73
17	24	-34
18	32	40
19	25	-20
21	20	23

h = 3, k = 11

0	48	44
2	123	-105
4	55	48
6	71	63
7	40	-43
8	83	-74
9	44	44
10	24	-25
12	94	106
14	66	66
16	53	-64

h = -3, k = 11

1	32	30
4	88	-88
6	135	-127
7	36	25
8	110	114
9	46	-38
10	35	-32
11	29	22
12	86	-92
14	69	-72
16	46	52
17	45	-39
18	40	-36

h = 3, k = 13

1	38	37
2	90	85
3	109	-102
4	25	11
5	76	-79
6	67	-81
7	62	67
9	48	-51
10	28	32
11	49	-47

h = -3, k = 13

2	83	-79
3	117	111
4	26	27
5	66	55
6	44	39
7	95	-96
9	68	59
11	31	33
12	31	28
14	28	-26
15	55	-64
17	54	51
18	19	23

h = 3, k = 15

0	19	11
2	71	76
3	52	57
5	43	44
6	36	-37
7	32	-33
8	22	-15
11	42	53
12	19	21

h = -3, k = 15

1	29	24
2	19	-13
3	63	-65
4	31	-23
5	19	-6
6	82	88
7	29	30
8	23	17
10	31	25
11	38	-42
14	42	40
15	19	16

h = 3, k = 17

2	22	21
3	45	46
5	35	35
9	16	24

h = -3, k = 17

1	16	-14
2	16	-11
3	23	-11
4	32	-30
5	40	-34
6	16	-17
7	34	34
9	30	-27
10	24	27
12	40	-42

h = 3, k = 19

2	26	-38
3	21	-28

h = -3, k = 19

1	31	7
3	41	47
4	33	-42
5	18	22
6	39	-49

h = 4, k = 0

0	61	46
2	114	119
4	242	284
6	107	-95
8	52	-55
10	75	81
12	109	112
14	47	-54
16	29	34
18	26	26

h = -4, k = 0

2	29	-73
4	110	194
6	31	47
8	101	98
10	25	-18
12	36	21
14	40	-36
16	24	-25
22	35	-40

h = 4, k = 2

1	109	-107
2	152	124
3	15	6
5	163	155
6	61	-60
7	112	-114
9	26	23
10	76	-88
11	53	54
13	64	82
14	47	53
15	44	-58
17	49	58
18	80	-106

h = -4, k = 2

1	70	79
2	90	-98
3	102	-116
4	24	-7
5	101	119
6	141	141
7	138	163
8	19	12
9	22	-18
10	46	31
12	29	-20
13	105	116
14	23	-26
15	75	74
17	48	-47
18	48	54
19	46	42
20	21	-15
21	40	41
22	40	-39

h = 4, k = 4

0	57	-52
1	88	75
2	108	-92
4	59	-57
5	95	-24
6	110	104
7	75	75
8	270	-248
10	78	-83
14	46	61
15	15	18
16	97	-125
17	17	-25
18	18	-23

h = -4, k = 4

1	55	-45
2	96	85
3	53	49
4	178	-199
5	27	-19
6	18	-18
7	57	-71
8	181	201
9	40	37
11	39	29
12	119	-142
13	32	-33
14	23	26
16	109	120
17	34	31
18	33	-37
20	14	1
21	18	-17
22	26	22

h = 4, k = 6

0	27	-18
1	104	87
2	188	163
3	86	78
4	64	58
5	94	-89
6	95	-87
7	77	73
9	40	36
11	30	-28
13	61	-81
14	30	35
15	40	49
16	28	32
17	31	-32

h = -4, k = 6

1	73	-67
2	176	-136
3	62	49
4	81	78
5	122	-110
6	116	117
7	67	-69
8	32	-32
11	16	11
12	32	36
13	41	-47
14	29	-35
15	42	-45
16	34	-34
17	33	30
18	55	63
19	15	-15
22	40	-49

h = 4, k = 8

0	28	13
1	30	-22
2	77	68
3	19	-17
4	200	182
5	98	93
6	79	-74
9	37	-37
10	27	28
11	27	31
12	95	106
13	57	64
14	20	-26
15	30	-38
16	38	48

h = -4, k = 8

1	16	-13
2	76	-63
3	51	-41
4	93	77
5	53	49
6	38	34
7	33	28
8	45	36
9	29	17
13	42	44
14	34	-27
15	48	46
16	16	-14
18	21	22
21	30	28

h = 4, k = 10

1	37	-33
3	40	34
4	43	-45
5	86	82
7	71	-78
8	54	-57
9	46	52
10	66	-75
11	33	34
12	15	-12
14	65	74
15	17	-22

h = -4, k = 10

1	72	67
2	65	-58
3	98	-90
4	64	-82
5	68	62
6	16	13
7	90	85
8	66	62
10	21	-19
12	64	-61
13	93	92
15	45	37
16	43	41
17	28	-29
18	18	17
19	49	42

h = 4, k = 12

0	63	-59
1	88	83
4	25	-19
5	45	-43
6	34	30
7	75	87
8	98	-114
10	28	-28
11	32	-42
12	17	23
14	34	42

h = -4, k = 12

1	76	-69
3	92	96
4	110	-105
5	68	-65
7	78	-80
8	47	46
9	24	23
11	53	51
12	73	-72
13	59	-72
15	19	-14
16	58	50
17	39	37

h = 4, k = 14

0	30	-23
2	94	96
3	57	61
4	56	70
5	27	-32
6	41	-52
7	23	27
8	19	10
10	48	55
11	16	22
12	30	39

h = -4, k = 14

2	89	-90
3	26	-23
4	42	47
5	34	-25
6	46	46
8	31	-28
10	15	-16
11	24	-24
12	14	23
13	19	15
14	24	-23
15	23	-21
16	29	-30

h = 4, k = 16

0	17	9

h = 5, k = 1

0	85	-81
1	78	-75
3	98	-97
4	94	88
5	74	64
6	76	-69
7	30	-18
8	48	-51
9	115	-116
10	24	28
11	17	-14
12	34	33
13	33	34
14	15	15
15	44	-53
16	17	15
17	51	-63

h = -5, k = 1

1	26	-38
2	75	-116
4	40	77
5	71	122
6	28	-37
7	23	-26
8	16	-21
9	17	-26
10	27	-33
11	14	-16
12	21	21
13	51	61
14	63	-68
15	49	-51
18	24	22
22	43	-46

h = 5, k = 3

0	43	43
1	69	-54
2	48	39
4	47	-41
6	101	96
7	62	-60
9	41	-34
10	59	-63
13	39	-37
14	47	61
17	12	-16

h = -5, k = 3

1	44	44
2	65	51
3	86	-81
4	107	-119
5	45	47
6	104	120
7	33	33
8	84	89
9	26	-41
11	53	-48
12	65	-80
13	61	64
14	76	85
16	35	43
17	34	-33
21	31	28
22	18	26

h = 5, k = 5

0	21	14
1	120	97
2	36	26
3	23	21
4	27	23
5	43	-37
6	33	25
7	64	63
9	67	69
10	36	-29
12	40	19
13	31	28
14	49	52
15	28	40

h = -5, k = 5

1	21	-19
2	34	-29
3	113	99
4	37	-30
5	115	-94
6	70	66
7	49	-54
8	28	30
9	45	47
11	70	66
12	40	-45
13	76	-90
14	35	37
15	30	28
17	47	52
18	32	23
20	13	-13
21	40	-33

h = 5, k = 7

0	144	-122
1	29	-25
2	20	15
3	57	55
4	91	88
5	47	-46
6	60	-58
8	86	-84
9	33	29
10	42	45
12	38	42
15	26	25

h = -5, k = 7

1	26	16
2	99	-80
3	32	22
4	69	60
5	62	-58
6	59	-50
7	56	50
8	50	-42
10	37	-30
12	24	17
14	78	-82
15	24	-29
16	17	9
17	19	-19

h = 5, k = 9

1	69	-65
3	110	-110
4	30	26
5	78	72
6	41	-35
7	50	-45
9	99	-117
10	33	-32
13	17	26
14	28	29

h = -5, k = 9

2	103	-83
3	72	-60
4	37	29
5	141	125
6	28	14
7	31	-32
8	40	32
9	34	-26
10	36	-30
13	54	59
15	46	-48
16	27	24
17	20	-16
18	19	15

h = 5, k = 11

1	29	31
2	37	33
5	29	24
6	80	76
7	59	68
8	23	20
9	84	-88
10	51	-53
11	20	21
5	42	-31
6	62	67
7	17	-16
8	24	-24
9	17	26
10	50	-58
13	25	-29

h = -5, k = 11

1	29	30
2	64	57
4	86	-79
5	47	-38
6	93	85
8	75	77
10	23	18
11	24	-20
12	75	-74
14	85	76
16	40	35

h = 5, k = 13

0	40	-44
1	50	56
2	42	46
3	17	19
4	23	17
5	18	-9
7	33	40
8	15	-21
9	33	37

h = -5, k = 13

1	24	-17
2	40	-43
3	48	50
5	61	-54
6	37	36
7	34	-31
8	35	-33
11	44	47
13	64	-51
15	28	21
16	17	-12

h = 5, k = 15

0	50	-55
1	34	-38
4	56	67
6	33	-40
7	14	-19
8	43	-57

h = -5, k = 15

2	50	-48
4	34	34
6	40	-47
7	29	30
9	22	-23
10	26	-21
13	23	17
14	38	-43

h = 5, k = 17

0	30	32
1	29	-32
2	14	15
3	26	-30

h = -5, k = 17

2	34	-34
3	28	-26
5	47	45
6	40	42
7	24	-21
8	38	34

h = 6, k = 0

0	256	-221
2	26	-28
4	111	124
6	20	22
8	175	-164
10	36	26

h = 6, k = 2

1	59	-48
2	37	33
5	29	24
6	80	76
7	59	68
8	23	20
9	84	-88
10	51	-53
11	20	21

h = 6, k = 4

0	60	47
3	28	-20
4	98	103
6	29	23
7	40	-35
8	84	84
10	36	-35

h = -6, k = 4

6	45	37
8	42	43
10	78	-61

h = 6, k = 6

0	67	-58
1	40	26
4	25	22
5	67	-68
6	35	35
7	58	-61
8	43	-44
9	67	81
10	48	-51
11	37	-30

h = -6, k = 6

1	139	137
2	54	-43
3	55	38
4	34	23
5	40	-31
6	39	40
7	57	48
8	44	-31
9	76	80
10	52	-29

h = 6, k = 8

0	150	-145
1	50	-41
3	40	-46
4	57	61
5	46	44
7	28	27
8	131	-131
9	59	-63
10	18	17

h = -6, k = 8

1	75	-70
2	19	17
4	44	50
5	51	46
6	35	-28
7	29	-31
8	32	-10
9	68	-53
10	37	28
11	38	21

h = 6, k = 10

0	47	50
1	34	-28
2	27	21
3	19	24
6	36	37
7	18	25
8	64	59
9	24	-27
10	52	-58

h = -6, k = 10

1	28	-24
2	58	-52
3	20	-20
4	18	-20
6	89	88
8	23	25
9	50	-40
10	67	-63
11	37	26

h = 6, k = 12

3	25	-14
4	48	54
6	15	19
7	26	-28
10	27	-36

h = -6, k = 12

1	54	49
2	26	-17
3	38	34
4	29	21
6	33	28
8	42	24
9	58	55
10	33	-24

h = 6, k = 14

0	59	-65
4	29	32
7	28	-37

h = -6, k = 14

1	51	62
4	44	34
7	40	33

h = 6, k = 16

0	36	-40
1	25	-30
2	12	12

h = 7, k = 1

0	72	-61
1	35	-25
2	19	8
3	35	-33
4	44	49
5	51	44
6	48	49
7	57	67
8	42	-46
9	35	-38
10	18	-18
11	24	16

h = 7, k = 3

0	27	16
2	39	-23
6	39	-29
7	36	39
8	21	20
9	28	14
10	43	-37

h = 7, k = 5

7	57	-65
9	19	-11
10	50	-49

h = 7, k = 7

0	61	-59
1	40	38
4	64	77
6	44	55
8	63	-61
9	23	24
11	26	-22

h = -7, k = 7

9	50	34
10	68	60

h = 7, k = 9

0	33	-26
1	38	-33
2	36	22
5	43	48
6	40	29
7	61	64
9	23	-28
10	15	-15

h = -7, k = 9

6	55	48
8	38	-22
9	61	-58
11	76	75

h = 7, k = 11

2	32	-18
6	19	-20
8	18	19

h = 7, k = 13

2	18	-18
4	20	19

h = 7, k = 15

0	36	-50

h = 8, k = 0

0	59	-56
2	38	-37
4	53	66
6	30	34

h = 8, k = 2

1	28	22
2	53	-45
3	71	-73
6	34	33
10	56	-57

h = 8, k = 4

0	70	-67
2	37	36
3	37	31
4	40	-33
6	23	-26
8	22	-13
10	18	16

h = 8, k = 6

1	26	14
2	55	-56
3	50	60
6	61	61

h = 8, k = 8

0	34	-34
2	36	-35
3	23	-28
4	50	59
6	22	19
8	16	16

h = 8, k = 10

1	21	21
3	32	-33
4	27	-26
6	16	15

h = 8, k = 12

0	28	-26
3	27	34

h = 9, k = 1

1	17	17
2	60	-56
3	31	-31
6	25	21

h = 9, k = 3

0	37	-28
1	33	39
2	58	42
3	26	-26
5	27	-18
6	21	11

h = 9, k = 5

1	54	-55
2	20	13
3	34	36
5	29	28
6	29	29

h = 9, k = 7

2	62	-65
5	17	-16

h = 9, k = 9

1	19	16
2	32	-23

h = 10, k = 0

0	21	16
2	25	-16

h = 10, k = 2

1	34	33
2	24	-22

h = 10, k = 4

0	15	-21
1	17	-15
2	16	17

h = 10, k = 6

0	14	12

Discussion of the molecular structure

The most interesting finding of this study is the binuclear nature of the ZTC molecules, which in the crystal would be represented by the dimeric formula, $Zn_2[S_2CN(CH_3)_2]_4$. This binuclear molecule is depicted in Fig. 1 in its *b*-axis projection. The asymmetric unit consists of the atoms numbered 1 to 13 (the half above the dotted line), and comprises one monomeric molecule of $Zn[S_2CN(CH_3)_2]_2$. The other half of the molecule is an identical asymmetric unit related to the first one by the twofold axis. The distorted tetrahedral coordination of sulfur atoms about each zinc atom is clearly shown. The asymmetric unit, in addition to its zinc atom, has two thiocarbamate (TC) groups, one wholly bound to the zinc atom of its tetrahedron and the other which acts as a link between the two ZnS_4 tetrahedra. The former will be designated as the chelating TC group, and the latter as the bridging TC group.

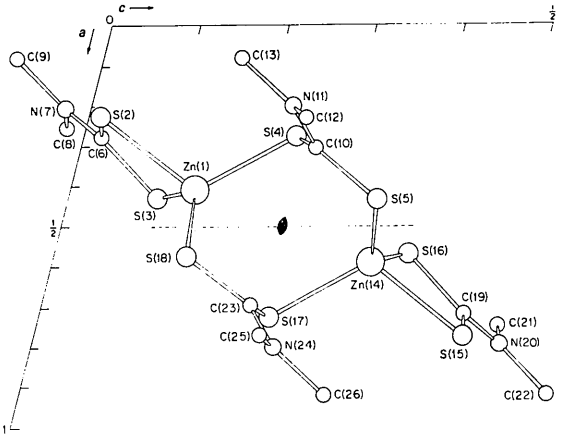


Fig. 1. Projection of the binuclear molecule along positive *b* as viewed from the origin. Atoms 1 to 13, above the dashed line, make up the asymmetric unit.

The bond distances and angles, other interatomic distances within the binuclear molecule, and their e.s.d.'s, are listed in Table 3. These values were calculated by the method of Cruickshank & Robertson (1953), with an IBM 1620 program (Chu, 1963). The values do not include the σ's of the lattice constants which on the average are two or more times better than those of the atomic parameters. The bond distances, bond angles, and other interatomic distances involving only zinc and sulfur atoms are determined with good precision, while those distances and angles involving the carbon and nitrogen atoms are considerably less precise. The precision, however, is comparable to that attained in previous metal dithiocarbamate studies (Table 4), except that BMVZ and BDMVZ achieved better precision. A comparison of interatomic and bond distances in the ZTC molecule with those in other metal dithiocarbamate molecules is summarized in Table 4.

The rather strong distortion from strict tetrahedral symmetry of the sulfur coordination around the zinc is very evident. The Zn–S distances in the tetrahedron

Table 2. *Fractional atomic coordinates, anisotropic thermal parameters*, and their estimated standard deviations, σ*

The σ's, in parentheses, have been multiplied by 10^4.

Zn(1)	0·4098 (4)	0·3604 (2)	0·1389 (1)
S(2)	0·2255 (7)	0·3631 (3)	0·0134 (2)
S(3)	0·4292 (7)	0·4997 (3)	0·0987 (3)
S(4)	0·2747 (7)	0·3693 (3)	0·2372 (2)
S(5)	0·4336 (7)	0·2384 (3)	0·3495 (3)
C(6)	0·2781 (27)	0·4676 (10)	0·0194 (9)
N(7)	0·2051 (24)	0·5257 (10)	−0·0299 (8)
C(8)	0·2559 (34)	0·6159 (13)	−0·0227 (12)
C(9)	0·0811 (34)	0·5006 (16)	−0·0979 (12)
C(10)	0·3032 (28)	0·2637 (11)	0·2654 (10)
N(11)	0·1994 (22)	0·2028 (9)	0·2271 (9)
C(12)	0·2306 (50)	0·1134 (13)	0·2461 (15)
C(13)	0·0770 (27)	0·2208 (14)	0·1548 (10)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn(1)	0·0119 (5)	0·0016 (1)	0·0011 (1)	0·0005 (2)	−0·0003 (1)	0·0004 (1)
S(2)	0·0158 (11)	0·0020 (2)	0·0013 (1)	−0·0008 (3)	−0·0014 (3)	0·0000 (1)
S(3)	0·0142 (9)	0·0018 (2)	0·0014 (1)	−0·0010 (3)	−0·0011 (3)	0·0002 (1)
S(4)	0·0134 (10)	0·0020 (2)	0·0013 (1)	0·0004 (3)	−0·0005 (3)	0·0000 (1)
S(5)	0·0129 (10)	0·0020 (2)	0·0015 (1)	−0·0010 (3)	−0·0009 (3)	0·0004 (1)
C(6)	0·0183 (43)	0·0010 (6)	0·0009 (5)	0·0010 (12)	−0·0019 (12)	0·0002 (4)
N(7)	0·0195 (39)	0·0021 (6)	0·0007 (4)	0·0013 (12)	−0·0014 (10)	0·0004 (4)
C(8)	0·0261 (58)	0·0024 (8)	0·0020 (7)	−0·0003 (16)	−0·0013 (16)	0·0015 (6)
C(9)	0·0207 (50)	0·0045 (11)	0·0015 (6)	0·0023 (20)	−0·0032 (14)	0·0005 (7)
C(10)	0·0194 (45)	0·0013 (6)	0·0012 (6)	−0·0015 (13)	−0·0012 (13)	0·0001 (5)
N(11)	0·0135 (33)	0·0009 (5)	0·0019 (5)	−0·0012 (10)	−0·0025 (10)	0·0001 (4)
C(12)	0·0484 (99)	0·0012 (8)	0·0032 (9)	−0·0035 (21)	−0·0020 (24)	0·0001 (7)
C(13)	0·0111 (38)	0·0040 (10)	0·0010 (6)	−0·0001 (15)	−0·0020 (12)	0·0007 (6)

* In the expression: $\exp\{-(h^2\beta_{11}+\ldots+2kl\beta_{23})\}$.

vary from 2·312 to 2·429 Å, in satisfactory agreement with the value, 2·35 Å, the sum of the Zn and S tetrahedral covalent radii (Pauling, 1960). Two of the six tetrahedral angles, however, S(3)–Zn(1)–S(2) = 76·37° and S(3)–Zn(1)–S(18) = 136·53°, differ greatly from the ideal value, 109·5°. An alternative interpretation of the coordination about the zinc atom is to consider it distorted trigonal bipyramidal as favored by BMVZ in the corresponding zinc diethyl compound. In this interpretation atoms S(3), S(4) and S(18) with the rather normal Zn–S distances of 2·333, 2·373 and 2·312 Å comprise the trigonal grouping around the zinc at the center of the bipyramid. It is to be noted (Table 3) that the corresponding S–Zn–S angles are distorted

Table 3. *Summary of interatomic distances and angles in the binuclear molecule*

Bond —, nonbond · · ·

	Distance	σ		Angle	σ
Zn(1) · · · Zn(14)	3·973 Å	0·006 Å	Zn(1) –S(2)—C(6)	81·98°	0·66°
Zn(1)—S(4)	2·373	0·006	Zn(1) –S(3)—C(6)	83·96	0·64
Zn(1)—S(2)	2·429	0·006	Zn(1) –S(4)—C(10)	96·51	0·69
Zn(1)—S(3)	2·333	0·006	S(2)—C(6) —S(3)	117·29	1·08
Zn(1)—S(18)	2·312	0·006	S(3)—Zn(1) –S(2)	76·37	0·19
			S(2)—Zn(1) –S(4)	113·73	0·20
Zn(1) · · · S(17)	3·036	0·006	S(2)—Zn(1) –S(18)	108·41	0·20
Zn(1) · · · S(5)	4·274	0·006	S(3)—Zn(1) –S(18)	136·53	0·21
Zn(1) · · · C(23)	3·020	0·020	S(3)—Zn(1) –S(4)	105·76	0·20
Zn(1) · · · C(10)	3·097	0·020	S(4)—Zn(1) –S(18)	110·70	0·20
Zn(1) · · · C(6)	2·764	0·020	S(2)—C(6) —N(7)	123·76	1·47
			S(3)—C(6) —N(7)	118·84	1·43
C(6)—S(2)	1·701	0·019	C(6) —N(7) —C(9)	120·18	1·75
C(6)—S(3)	1·748	0·019	C(6) —N(7) —C(8)	121·88	1·72
C(6)—N(7)	1·325	0·025	C(8) —N(7) —C(9)	117·68	1·75
N(7)—C(8)	1·479	0·029			
N(7)—C(9)	1·464	0·030	S(4)—C(10) –S(5)	120·18	1·17
			S(4)—C(10) –N(11)	119·69	1·46
C(10)—S(4)	1·739	0·020	S(5)—C(10) –N(11)	119·03	1·47
C(10)—S(5)	1·699	0·021	C(10) –N(11) –C(12)	120·07	1·84
C(10)—N(11)	1·368	0·026	C(10) –N(11) –C(13)	122·29	1·62
N(11)—C(12)	1·458	0·034	C(12) –N(11) –C(13)	116·09	1·78
N(11)—C(13)	1·487	0·026			
			C(10) –S(5)—Zn(14)	96·51	0·71
S(2) · · · S(4)	4·022	0·007	S(2) · · · S(3) · · · S(17)	101·28	0·18
S(2) · · · S(3)	2·945	0·007	S(3) · · · S(2) · · · S(18)	77·63	0·16
S(2) · · · S(18)	3·846	0·007	S(18)—Zn(1) · · · S(17)	66·14	0·20
S(3) · · · S(18)	4·315	0·007			
S(3) · · · S(4)	3·752	0·007			
S(4) · · · S(18)	3·854	0·007			
S(4) · · · S(17)	3·718	0·007			
S(5) · · · S(18)	4·083	0·007			
S(4) · · · S(5)	2·980	0·007			
S(3) · · · S(17)	3·964	0·007			
C(10) · · · C(23)	3·515	0·028			
C(12) · · · C(25)	4·522	0·028			
C(13) · · · S(18)	4·167	0·019			
N(11) · · · N(24)	4·937	0·03			

Table 4. *Comparison of bond distances in various dialkyldithiocarbamates*

Mean values of the bonds in the dithiocarbamate groups

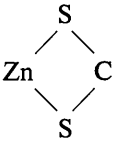
Dithiocarbamate	S–C (Å)	C=N (Å)	N–C (Å)
Co(NO) dimethyl	1·75	1·25	1·5
Cu(I) diethyl	1·708 ± 0·018	1·408 ± 0·033	1·483 ± 0·025
Cu(II) diethyl	1·717 ± 0·004	1·34 ± 0·01	1·470 ± 0·005
Ni(II) diethyl	1·707 ± 0·005	1·33 ± 0·01	1·485 ± 0·011
Zn diethyl	1·727 ± 0·005	1·325 ± 0·009	1·473 ± 0·007
Zn dimethyl (this study)	1·722 ± 0·010	1·347 ± 0·018	1·472 ± 0·015

Zn–S distances in dialkyldithiocarbamates

Zn dimethyl	Zn diethyl
2·312 ± 0·006 Å	2·331 ± 0·003 Å
2·333 ± 0·006	2·355 ± 0·003
2·373 ± 0·006	2·383 ± 0·002
2·429 ± 0·006	2·443 ± 0·003
3·036 ± 0·006	2·815 ± 0·002

considerably from the ideal value, 120°, and it is evident that the zinc atom is out of the plane of the sulfur atoms. The Zn(1)–S(2) and Zn(1)–S(17) distances, 2·429 and 3·036 Å respectively, are the axial bonds in a trigonal bipyramidal configuration. The Zn–S(2) bond is only slightly longer than the Zn–S(3), Zn–S(4), and Zn–S(18) of the Zn(1) tetrahedron. The Zn–S(17) distance, however, is so much larger than the Zn–S(2) distance that it can in no sense be considered an equivalent distance in a coordination configuration. The author thus favors the tetrahedral coordination interpretation.

The strongly distorted S(3)–Zn(1)–S(2) angle is a part of the interesting four-membered



ring formed by the chelating TC group and the Zn(1) atom (Fig. 2, molecule I). The angles about the sp^2-type C(6) atom are not greatly different from the expected 120° value, that in the ring being 117·3°. The angles at the S(2) and S(3) atoms, 82·0 and 84·0°, respectively, are in excellent agreement with the corresponding angles observed by BMVZ in the corresponding ring in the zinc diethyl compound. How much distortion these angle values represent for the bond angle at a sulfur atom depends upon what one considers the normal sulfur bond angle. The angle S–S–S in the S_8 molecule of rhombic sulfur is 105° (Warren & Burwell, 1935; Lee & Donohue, 1944), and might be considered the normal angle. The sulfur bond angle then becomes successively smaller as one passes to smaller and smaller rings. The C–S–C angle in the six-membered 1,4-dithiin, $C_4H_4S_2$, ring (Howell, Curtis & Lipscomb, 1954) is reported to be 100°; it is reported to be 91° in the five-membered rings of both thiophene, C_4H_4S (Schomaker & Pauling, 1939), and 1,4-thiophthene,

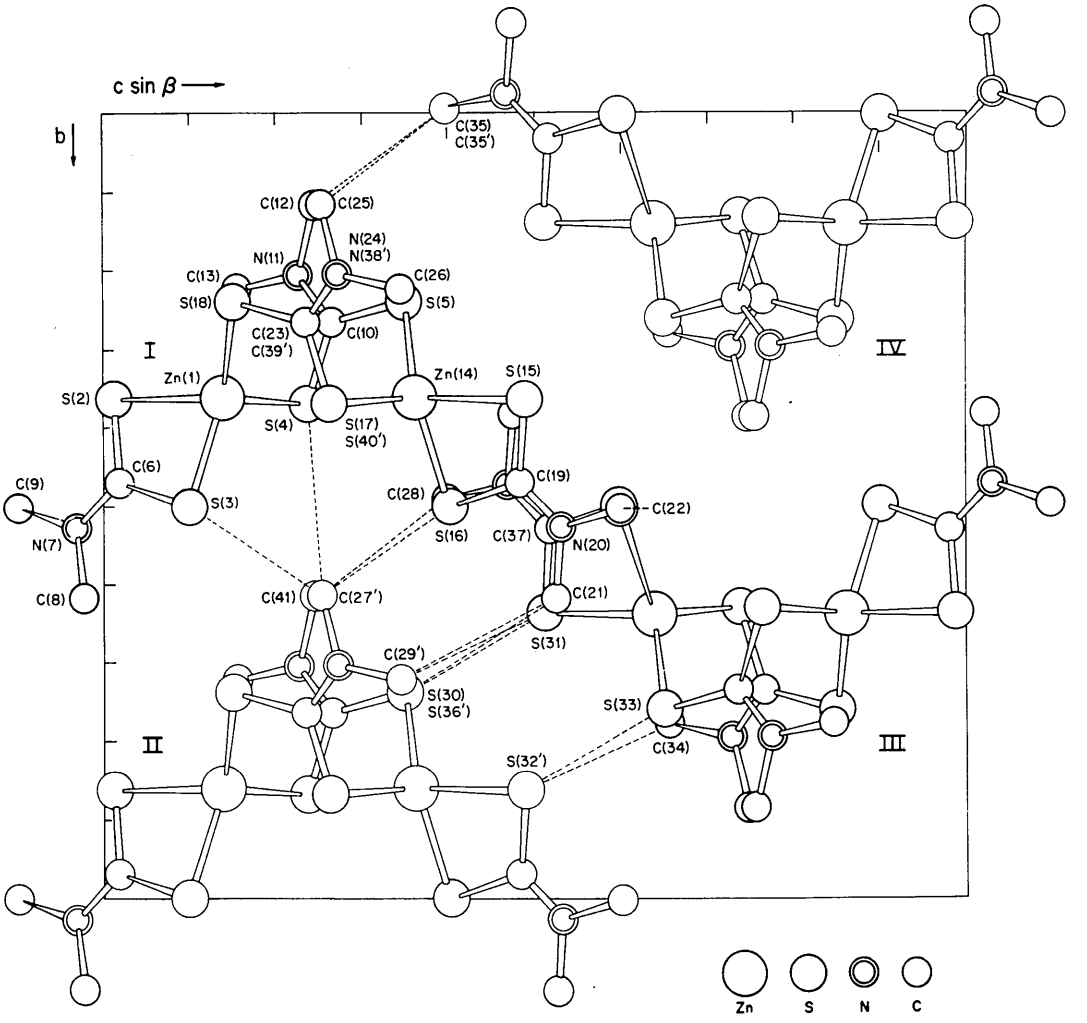
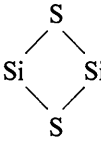


Fig. 2. Projection of the unit cell along *a*. Positive *a* extends perpendicularly from the plane of the paper, and the molecules are viewed looking along positive *a* toward the origin. Molecules I and III lie on twofold axes at $a=-0{\cdot}5$ or $+0{\cdot}5$, and molecules II and IV on twofold axes at $a=0$ or 1·0. Primed atoms relate to molecules on axes at $a=-0{\cdot}5$ or 0, unprimed atoms to molecules on axes at $a=0{\cdot}5$ or 1·0. Dashed lines refer to some of the intermolecular distances presented in Table 7.

$C_6H_4S_2$ (Cox, Gillot & Jeffrey, 1949); and in the four-membered ring in tetramethylcyclodisilthiane, $(CH_3)_2$-



Si Si-$(CH_3)_2$, the Si–S–Si angle is reported as 75° (not very accurate) (Yokoi, Nomura & Yamasaki, 1955). The C–S–Zn angle of ~83° in the ZnS_2C ring is thus about what would be expected.

The extreme distortion in the ring occurs in the S–Zn–S angle, 76·4°, which is reduced from the ideal tetrahedral value, 109·5°, by ring closure. A compensating effect seems to take place in the neighboring angle S(3)–Zn(1)–S(18) of the ZnS_4 tetrahedron which has increased from the expected 109·5° to 136·5°. Possibly ZTC forms the binuclear molecule in the crystal to avoid similar severe distortion of two additional angles of the ZnS_4 tetrahedron. Thus angle S(4)–Zn(1)–S(18) retains the nearly normal tetrahedral value, 110·7°, whereas in a monomer molecule this angle would be expected to be distorted to a value comparable to that of angle S(3)–Zn(1)–S(2), 76·4°. Malatesta (1965) reported that the diethyl compound has a normal (monomeric) molecular weight in benzene. ZTC, likewise, by vapor pressure osmometry in chloroform solution was observed to be monomeric*. Since both compounds in the crystal form binuclear molecules with similar angles in the ZnS_2C rings, it appears that the molecules in solution can tolerate more distortion. The ZnS_2C rings (Fig. 1) show moderate deviation of the atoms from a plane.

The central eight-membered ring in the binuclear molecule deserves brief comment. It is comprised of atoms 1, 4, 10, 5, 14, 17, 23, and 18 (Fig. 1), and is shown in its *a*-axis projection in Fig. 3. It is to be noted that it has the 'cradle' form rather than the 'crown' form possessed by the S_8 molecule (Warren & Burwell, 1935). The eight angles in the ring vary from 96·5° to 120·2°. Although the average of these eight angles is 105·8° (angle S–S–S in S_8 is 105°) they are of three distinct types and the differences are real, the maximum σ being 1·17° for angle S(18)–C(23)–S(17). The Zn(1) and Zn(14) atoms are at a distance of 3·973 Å apart and on opposite sides of the ring. Since the single bonded Zn–Zn distance predicted from metallic radii (Pauling, 1960) would be about 2·50 Å, it is evident that no metal–metal bond is present here.

Fig. 4 presents the mean values of the angles and bond distances in the dimethyldithiocarbamate groups, and Table 4 presents a comparison of bond distances in various dialkyldithiocarbamates. The bond distances in ZTC are in quite satisfactory agreement with those of other metal dialkyldithiocarbamates recently studied. A similar comparison of bond angles is equally satisfactory. The S–C bond length seems normal for a carbon atom with sp^2 hybridization (see Dias & Truter, 1964). The C=N bond of 1·347 Å is so depicted to indicate that it has a high percentage of double bond character. Its LCAO-MO double bond order $p=0{\cdot}58$, as calculated from Coulson's (1939) C–C formula modified by Liquori & Vaciago (1956) for the C–N bond:

$$B=S-\frac{S-D}{1+0{\cdot}6625(1-p)/p}$$

where

B = observed C=N bond distance, 1·347 Å,
S = single bond distance, 1·472 Å,
D = double bond distance, 1·287 Å } (Pauling, 1960).

The chelating TC group appears to deviate less from planarity than the bridging TC group (Fig. 1). Calculations of the least-squares planes, however, were not conclusive because of the moderately high σ's of some of the atoms involved.

Analysis of the thermal motion

The β_{ij}'s (Table 2) were used to calculate the thermal vibration ellipsoids of the atoms, the rigid-body translational tensor τ, and the librational tensor ω, with an IBM 7090 program of Gantzel, Coulter & Trueblood adapted to the Michigan system by Shiono (1964). The observed U_{ij}'s of the atoms relative to an orthogonal

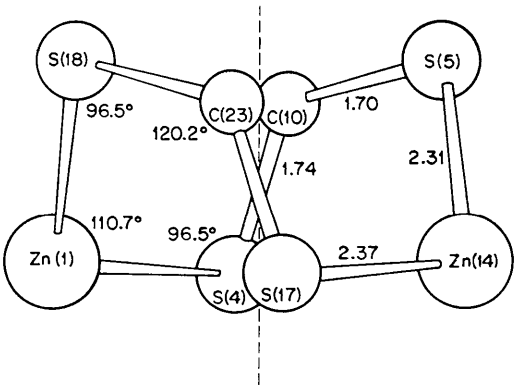


Fig. 3. Projection along the *a* axis of the central eight-membered ring of the binuclear molecule. The ring has two identical halves related by a twofold axis (depicted as a dashed line) parallel to **b**. Angles are given in degrees and bond distances in Å.

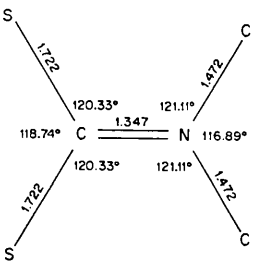


Fig. 4. Mean values of the angles and bond distances (Å) in the dimethyldithiocarbamate groups.

* Physical Measurements Laboratory, Mellon Institute.

set of axes parallel to a, b, and c^* (Table 5) were calculated by procedures of Cruickshank (1956) and Rollett & Davies (1955). At the same time the principal axes of the atomic ellipsoids and their direction cosines were determined (not presented here). The **U** tensors for each atom were calculated from the τ and ω tensors, and provide the calculated U_{ij}'s of Table 5. The r.m.s. difference between the observed and calculated U_{ij}'s is 0·0117 Å^2, a value which indicates that interpretation in terms of rigid-body vibrations is not justified. Indeed, there are 27 cases where $|\Delta U_{ij}|$ is $\gtrsim 0{\cdot}5\ U_{ij}$ (obs.). The above r.m.s. value corresponds to an e.s.d., σU_{ij} (obs.), of $0{\cdot}0117 \times (78/66)^{\frac{1}{2}} = 0{\cdot}0127$ Å^2, since 12 parameters τ_{ij} and ω_{ij} were determined from $13 \times 6 = 78$ independent U_{ij}'s. The U_{ij}'s, of course, will be affected further by errors (not taken into account) due to absorption and extinction.

Inspection of Fig. 1 reveals that the orthogonal axes parallel to a, b, and c^* are quite suitable axes for the description of the binuclear ZTC molecules. Since the principal axes of the atomic ellipsoids generally make relatively small angles with the orthogonal set of axes, the observed U_{ij}'s of Table 5 give an approximate picture of the atomic vibrations. For most of the atoms the predominant component of their vibrations is approximately along the a direction. It might be claimed that the geometry of this molecule would intuitively lead one to conclude that it would not vibrate as a rigid body. It is believed useful, however, to see this substantiated by the actual analysis.

Intermolecular distances

The van der Waals contacts between molecules are summarized in Table 6. All carbon atoms in Table 6 are methyl (Me) carbon atoms except C(10), C(37), and C(39). For comparison with the observed distances the expected distances are: S···Me ≧ 3·85 Å, S···S ≧ 3·70 Å, Me···Me ≧ 4·00 Å, C···N ≧ 3·20 Å, and N···N ≧ 3·00 Å (Pauling, 1960). All intermolecular distances are completely satisfactory. Several intermolecular distances have been indicated on Fig. 2.

Table 6. *Summary of closest intermolecular distances*

S(3) ···C(27′)	3·89 Å	S(4) ···S(40′)	4·79 Å
S(4) ···C(27′)	3·86	S(31) ···S(36′)	3·73
S(16) ···C(27′)	3·67	S(32′) ···S(33)	3·73
S(16) ···C(28)	4·14		
S(30) ···C(21)	4·36	C(10) ···C(39′)	5·01
S(30) ···C(29′)	4·31	C(12) ···C(35)	3·98
S(31) ···C(21)	4·36	C(21) ···C(29′)	4·02
S(31) ···C(29′)	4·08	C(25) ···C(35)	3·92
S(32′) ···C(34)	4·08	C(27′) ···C(28)	3·92
		C(27′) ···C(41)	3·94
N(11) ···N(38′)	3·68	C(37) ···N(20)	4·33

The author expresses his thanks and appreciation to Dr Marjorie Harding for relinquishing her further interest in determining the structure of ZTC, and to Mr Wayne Orr for preparing most of the photographs and measuring the reflection intensities. Thanks also are expressed to Dr A. Vaciago for providing a copy of his manuscript on zinc diethyldithiocarbamate in advance of its publication.

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Table 5. *Observed and calculated U_{ij}*

(In 10^{-4} Å^2)

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Zn(1)	454	529	196	98	179	168	14	0	−69	−132	63	−1
S(2)	644	551	256	248	213	170	−52	−1	−163	−140	2	−1
S(3)	574	726	232	148	225	222	−75	−55	−142	−166	21	69
S(4)	519	523	250	195	212	174	30	6	−95	−133	1	−1
S(5)	519	695	256	167	235	217	−85	−114	−128	−160	59	57
C(6)	750	661	120	231	145	200	58	3	−183	−157	23	69
N(7)	768	834	268	317	110	246	69	29	−133	−192	59	126
C(8)	1023	1224	296	301	323	355	−80	−18	−187	−260	213	203
C(9)	896	778	561	479	239	228	139	70	−307	−186	68	125
C(10)	763	630	158	192	194	203	−103	−121	−141	−151	12	27
N(11)	609	799	114	294	299	255	−82	−255	−266	−185	8	37
C(12)	1872	1188	151	271	508	363	−241	−377	−289	−255	21	67
C(13)	493	746	506	423	163	244	−30	−271	−193	−180	98	10

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The Crystal Stucture of Bis-(*N*-isopropyl-3-methylsalicylaldiminato)nickel

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(*Received* 19 *January* 1966 *and in revised form* 14 *March* 1966)

The crystal structure of bis(*N*-isopropyl-3-methylsalicylaldiminato)nickel, $Ni(C_{11}H_{14}NO)_2$, has been determined from three-dimensional integrating Weissenberg data. The cell has dimensions $a=11{\cdot}209$, $b=9{\cdot}979$, $c=9{\cdot}520$ Å, $\beta=107°31'$, space group $P2_1/c$, and contains two molecules.

The nickel atoms show planar coordination. Comparison of the molecular structure with that of bis(*N*-isopropylsalicylaldiminato)nickel shows the steric factors which cause the tetrahedral configuration to appear for *N*-sec-alkyl substituted salicylaldimine chelates, but gives no clue as to the reason for the planar configuration of the 3-methyl chelate.

Introduction

The crystal structures of chelates of nickel(II) and ring-substituted salicylaldimines are currently of considerable interest. Holm & Swaminathan (1963) have determined that for 3-substituted bis(*N*-isopropylsalicylaldiminato)nickel the magnetic moments are 3·28, 0 and 3·30 B.M. for the substituents hydrogen, methyl and ethyl, indicating the coordination configurations tetrahedral, planar and tetrahedral, respectively. The coordination configuration of the 3-hydrogen chelate has indeed been shown to be tetrahedral (Fox, Orioli, Lingafelter & Sacconi, 1964). We have now completed the structural determination of the 3-methyl chelate by three-dimensional X-ray diffraction techniques.

Experimental

The bis(*N*-isopropyl-3-methylsalicylaldiminato)nickel was prepared by the method of Sacconi, Paoletti & Del Re (1957) using 3-methylsalicylaldehyde, which was prepared according to the general procedure of the