Table 7. *Shortest intermolecular distances for crystals of betaine hydrochloride*

The equivalent position numbers are 1 for x,y,z; 2 for $x,\frac{1}{2}-y,\frac{1}{2}+z$; 3 for $-x,-y,-z$; and 4 for $-x,\frac{1}{2}+y,\frac{1}{2}-z$.

Atom 1	Atom 2	Distance	Position number of atom 2	Atom 2: translations in x	y	z
Cl	H(10)	2·79 (2) Å	3	1	1	2
	H(11)	2·80 (2)	2	0	0	0
	H(2)	2·88 (2)	2	−1	0	0
	H(6)	2·88 (2)	3	1	1	2
	H(7)	2·89 (2)	2	−1	0	0
	H(5)	3·02 (2)	2	−1	0	0
	H(8)	3·18 (2)	3	1	1	2
	H(3)	3·20 (2)	2	0	0	0
	H(9)	3·21 (2)	4	1	−1	1
	H(4)	3·26 (2)	1	−1	0	0
	H(8)	3·42 (2)	4	1	−1	1
C(1)	O(1)	3·270 (3)	4	1	−1	1
	O(2)	3·348 (3)	2	0	0	−1
C(2)	O(1)	3·440 (3)	1	1	0	0
C(4)	O(2)	3·459 (3)	4	1	0	1
O(1)	O(1)	3·396 (3)	3	1	1	2

References

Canepa, F. G., Pauling, P. & Sörum, H. (1966). *Nature, Lond.* **210**, 907.

Clastre, J. (1964). *C. R. Acad. Sci. Paris*, **259**, 3267.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321.

Hurst, R. P. & Matsen, F. A. (1959). *Acta Cryst.* **12**, 7.

Jellinek, F. (1957). *Acta Cryst.* **10**, 277.

Johnson, C. K. (1965). *ORTEP, A Fortran Thermal-Ellipsoidal Plot Program for Crystal-Structure Illustrations.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Senko, M. E. & Templeton, D. H. (1960). *Acta Cryst.* **13**, 281.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Tolbert, B. M., Adams, P. T., Bennett, E. L., Hughes, A. M., Kirk, M. R., Lemmon, R. M., Noller, R. M., Ostwald, R. & Calvin, M. (1953). *J. Amer. Chem. Soc.* **75**, 1867.

Acta Cryst. (1970). B**26**, 1397

The Crystal and Molecular Structure of 4-Formylpyridine Thiosemicarbazone

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4-Formylpyridine thiosemicarbazone, $C_7H_8N_4S$, forms pale yellow, acicular, monoclinic crystals. The space group is $P2_1/n$ and there are four molecules in the unit cell of dimensions $a=7{\cdot}238$, $b=13{\cdot}949$, $c=8{\cdot}419$ Å and $\beta=90{\cdot}9°$. The structure was solved from a minimum Patterson function and refined by Fourier syntheses and full-matrix least-squares methods. The final residual, R, for the 1339 observed reflections measured with a diffractometer is 0·055. The C–S bond distance of 1·678 (2) Å is comparable with that found in similar compounds. The N–N bond length of 1·365 (6) Å is interpreted in terms of resonance of the side chain with the pyridine ring. The molecules are linked by N–H$\cdots$S hydrogen bonds into dimer-like units which are held together by N–H$\cdots$N hydrogen bonds.

Introduction

Thiosemicarbazones possess a wide range of biological activity depending on the parent aldehyde or ketone. Hagenbach & Gysin (1952) reported that 4-formylpyridine thiosemicarbazone (4FPYTSC) showed tuberculostatic activity; subsequently, Jones, Slack, Squires & Wooldridge (1965) reported that it showed antiviral activity as well. However, French & Blanz (1966) showed that 4FPYTSC shows no carcinostatic activity whereas they found that 2-formylpyridine thiosemicarbazone was a tumor inhibitor. Apparently the position of the thiosemicarbazone group on the pyridine nucleus dictates the biological activity of formylpyridine thiosemicarbazones. Whether the differences in biological activities are related to electronic or steric effects is debatable. Therefore, a crystal structure study of 4FPYTSC was undertaken as part of a broad program which will attempt to correlate the biological activities of thiosemicarbazones with their molecular structure.

Experimental

A sample of 4FPYTSC was kindly supplied by F. A. French and recrystallized as pale yellow needles from warm ethanol. A crystal was cleaved to give a parallelepiped of dimensions approximately 0·08 × 0·13 × 0·15 mm and mounted with its long dimensions (the c axis) parallel to the φ axis of a General Electric single-crystal orienter. The unit-cell dimensions were obtained from a least-squares fit to twelve 2θ values measured using a narrow beam (1° take-off angle) of Cu $K\beta$ ($\lambda = 1{\cdot}39217$ Å) radiation.

$C_7H_8N_4S$, M. W. = 180·23, monoclinic,
$a = 7{\cdot}238(2)$, $b = 13{\cdot}949(3)$, $c = 8{\cdot}419(3)$ Å,
$\beta = 90{\cdot}87(4)°$,
$D_m = 1{\cdot}408$ g. cm^{-3}, $D_c = 1{\cdot}400$ g. cm^{-3},
$Z = 4$, space group $P2_1/n$ (C_{2h}^5), from systematic absences.

For collecting intensities, a take-off angle of 3·7°, which produces a wide beam, was used in measuring 4923 reflections with $2\theta \leq 130{\cdot}0°$ (Cu radiation, $\lambda = 1{\cdot}54051$ Å). A 20 sec count was taken for each reflection with the crystal and counter stationary. A 0·7 mil nickel foil was placed in front of the scintillation counter window. Four standard reflections were checked after every 100 reflections and showed no apparent change with time. Background corrections were made by measuring the background at various points in the hemisphere and averaging the values obtained at a given 2θ setting. A total of 1413 independent reflections was obtained after averaging equivalent reflections, of which 1339 were greater than 1·2 times the background and were considered to be observed. The remaining 74 reflections were set to one-half the minimum observable counts and coded as unobserved. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by application of the Lorentz–polarization corrections.

Determination and refinement of the structure

A sharpened three-dimensional Patterson function with the origin peak removed was used to locate the position of the sulphur atom. All but one ring carbon atom could then be located in a minimum Patterson function calculated on the basis of the known sulphur–sulphur inversion vector. A subsequent Fourier synthesis confirmed the position of the missing ring carbon atom. A second Fourier synthesis was computed in which all twelve independent atoms were used in the structure factor calculation. Atomic coordinates from this electron density map were used as starting parameters for a least-squares refinement. The value of R, the usual residual, was 0·179 for the 1339 observed reflections.

The full matrix was calculated in all least-squares cycles in which $\sum w(\Delta F)^2$ was minimized. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme: $\sqrt{w} = 1{\cdot}0$ if $F_o < 37$ and $\sqrt{w} = 37/F_o$ if $F_o > 37$, where F_o is on the same scale as in Table 4, was used in all least-squares calculations. After four cycles with individual isotropic thermal parameters, R was 0·134 and after four cycles with individual anisotropic thermal parameters, R was 0·077. A difference Fourier synthesis was then calculated and the eight hydrogen atoms were easily located; their coordinates are given in Table 1. The contributions of the hydrogen atoms, each with an isotropic temperature parameter, B, one unit greater than the average value of B for the atom to which it is bonded, were included in two additional least-squares cycles but the hydrogen atom parameters were not varied.

The largest shift in the final cycle was 0·00003 Å [for the y coordinate of C(1)], with an average shift of 0·00001 Å. The final R was 0·055. The positional parameters are given in Table 2 and the thermal parameters in Table 3. The observed structure amplitudes together with those calculated using the parameters given in Tables 1, 2 and 3 are listed in Table 4.

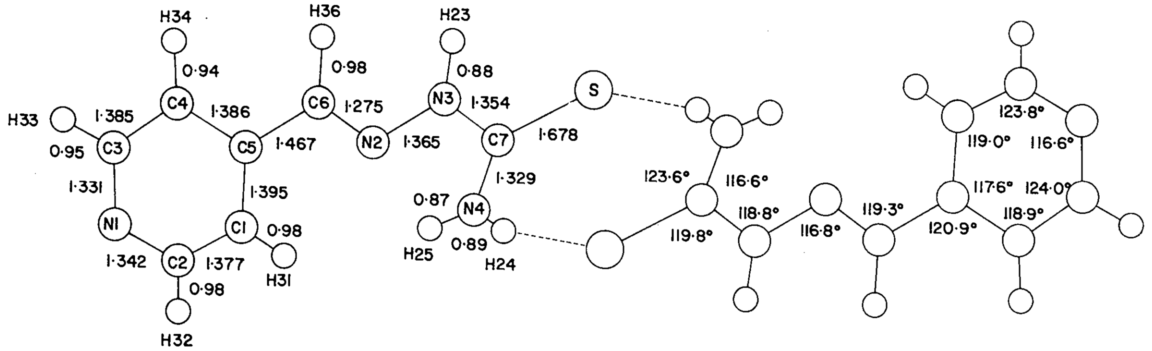

Fig. 1. Bond distances (Å) and angles (°). The estimated standard deviations of the bond distances average about 0·003 Å and those of the bond angles about 0·2°.

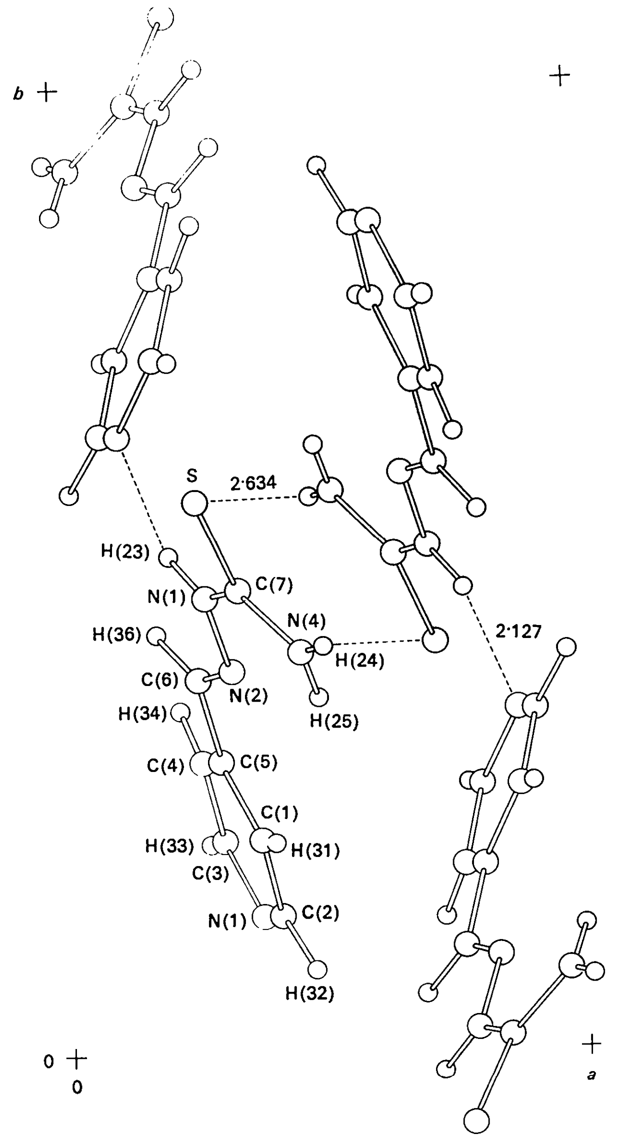

Fig. 2. Projection of the 4-formylpyridine structure on the (001) plane.

Table 1. *Hydrogen atom positions*

The hydrogen atom is given followed by the positional parameters times 10^3, peak height in e.Å^{-3}, and the temperature factor B (isotropic) used in the structure factor calculation.

	x	y	z	Peak height	B
H(23)	207	517	48	0·6	4·04
H(24)	510	422	390	0·6	4·95
H(25)	497	370	229	0·5	4·95
H(31)	401	218	−49	0·6	4·15
H(32)	453	84	−208	0·6	4·46
H(33)	266	217	−589	0·6	4·65
H(34)	213	356	−446	0·6	4·60
H(36)	178	437	−184	0·7	4·23

Table 2. *Final positional parameters and their estimated deviations (in parentheses)**

	x	y	z
S	27075 (9)	57229 (4)	35807 (7)
N(1)	3692 (3)	1409 (1)	−4151 (2)
N(2)	3256 (3)	3947 (1)	60 (2)
N(3)	2777 (3)	4734 (1)	925 (2)
N(4)	4643 (3)	4160 (2)	2918 (3)
C(1)	3737 (3)	2209 (2)	−1628 (3)
C(2)	4078 (3)	1430 (2)	−2587 (3)
C(3)	2952 (4)	2199 (2)	−4778 (3)
C(4)	2569 (3)	3020 (2)	−3918 (3)
C(5)	2969 (3)	3034 (1)	−2303 (3)
C(6)	2571 (3)	3884 (2)	−1340 (3)
C(7)	3450 (3)	4825 (2)	2427 (3)

* Values for all atoms times 10^4 (except for the sulphur atom, which is 10^5).

Discussion

The atomic numbering, bond distances and angles in the 4FPYTSC molecule are illustrated in Fig. 1. The thiosemicarbazone side chain is in the fully extended conformation as shown in the Figure. The pyridine ring is planar (see Table 5) but the side chain is bent out of the plane and twisted by 14°26′ with respect to the plane of the ring. This twist is less than the twist of 26° found in benzamide by Penfold & White (1959) but the C–N non-bonded distances of 2·834 ± 0·003 Å in 4FPYTSC and 2·83 Å in benzamide are identical. The nonplanarity is apparently a result of steric strain

Table 3. *Final thermal parameters and their estimated standard deviations*

All values have been multiplied by 10^4. The temperature factor for an atom is of the form:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	217 (2)	47 (1)	106 (2)	34 (1)	−57 (2)	−40 (1)
N(1)	175 (4)	40 (1)	122 (3)	3 (3)	−27 (5)	−20 (3)
N(2)	156 (4)	32 (1)	105 (3)	−4 (3)	−18 (5)	−11 (2)
N(3)	179 (4)	34 (1)	99 (3)	2 (3)	−47 (5)	−12 (2)
N(4)	230 (5)	57 (1)	112 (3)	64 (4)	−77 (6)	−24 (3)
C(1)	164 (4)	34 (1)	113 (3)	−7 (3)	−48 (6)	4 (3)
C(2)	179 (5)	34 (1)	134 (4)	4 (3)	−49 (6)	1 (3)
C(3)	211 (5)	46 (1)	112 (4)	0 (4)	−65 (6)	−14 (3)
C(4)	210 (5)	38 (1)	122 (4)	4 (4)	−72 (6)	−13 (3)
C(5)	142 (4)	32 (1)	108 (3)	−24 (3)	−30 (6)	−17 (3)
C(6)	176 (5)	32 (1)	111 (4)	−2 (3)	−57 (6)	−25 (3)
C(7)	151 (4)	37 (1)	102 (3)	−14 (3)	−13 (6)	−28 (3)

between N(2) and C(1). The entire side chain C(6)-N(2)-N(3)-C(7)-S-N(4) is only approximately planar. The groups C(6)-N(2)-N(3)-C(7) and N(3)-C(7)-S-N(4) are both planar but make an angle of 5°20′ with respect to each other. A similar twisting of the thiosemicarbazone chain in 2-keto-3-ethoxybutyraldehyde bis(thiosemicarbazone), KTS, was reported by Gabe, Taylor, Glusker, Minken & Patterson (1969). This twisting is probably a steric effect which increases the N(2) to N(4) nonbonded distance to 2·610 ± 0·003 Å.

A comparison of the C–S bond length in 4FPYTSC with that in related compounds is presented in Table 6. The C–S bond length in a thiosemicarbazone has been measured six times with an average value of 1·690 ± 0·005 Å and a range from 1·682 to 1·698 Å. Using the criteria suggested by Cruickshank & Robertson (1953), our value of 1·678 ± 0·002 Å is not significantly different ($t_0 = 2{\cdot}2$) from the mean value.

The average C–S distance in thiosemicarbazones of 1·690 Å agrees very well with the C–S distance in related compounds. In all cases the C–S distance is intermediate between a C–S single bond distance of 1·82 Å and the C–S double bond value of 1·56 Å quoted by Sutton (1965). Therefore, the C–S bond in thiosemi-

Table 4. *Observed and calculated structure amplitudes*

The three columns in each group contain the values, reading from left to right, of h, $10F_o$ and $10F_c$. A negative F_o indicates an unobserved reflection which was not included in the least-squares refinement.

H	FO	FC
K= 0, L= 0		
2	1063	-1236
4	285	280
6	105	-108
8	67	63
K= 0, L= 2		
-8	49	-45
-6	120	118
-4	21	-13
-2	243	-243
0	303	-302
2	332	-327
4	19	18
6	47	-46
8	26	23
K= 0, L= 4		
-6	115	112
-4	156	-153
-2	75	73
2	662	661
4	366	-381
6	268	282
K= 0, L= 6		
-6	14	-10
-4	136	138
-2	100	-111
0	19	-10
2	46	-33
4	31	-28
6	11	13
K= 0, L= 8		
-4	32	29
-2	93	-106
0	175	229
2	265	-280
4	125	128
K= 1, L= 0		
1	293	296
2	611	780
3	221	-215
4	105	-100
5	323	318
6	13	-8
7	86	-89
8	9	-6
K= 1, L= 1		
-8	-4	7
-7	48	50
-6	18	-16
-5	8	-1
-4	67	68
-3	293	286
-2	616	644
-1	257	-251
0	273	-265
1	274	-266
2	302	-357
3	349	347
4	192	188
5	-6	0
6	121	-128
7	50	50
8	31	32
K= 1, L= 2		
-8	74	-24
-7	75	-71
-6	33	34
-5	66	67
-4	38	38
-3	155	-153
-2	304	298
-1	255	244
0	244	-225
1	523	-525
2	229	254
3	120	118
4	246	-244
5	168	-170
6	54	59
7	31	33
8	-4	0
K= 1, L= 3		
-8	56	-51
-7	21	14
-6	60	61
-5	40	-38
-4	253	-247
-3	172	166
-2	165	161
-1	376	-378
0	518	-485
1	267	249
2	172	186
3	151	-142
4	17	15
5	36	35
6	37	-38
7	90	-89
8	58	58
K= 1, L= 4		
-7	113	106
-6	113	-113
-5	159	-164
-4	136	136
-3	125	125
-2	82	-82
-1	159	-148
0	353	-315
1	352	324
2	201	190
3	202	-186
4	53	-57
5	92	94
6	90	94
7	118	120
K= 1, L= 5		
-7	-5	11
-6	83	-83
-5	48	-51
-4	60	66
-3	-6	7
-2	149	156
-1	87	84
0	44	38
1	135	-108
2	16	19
3	10	-10
4	43	-37
5	84	87
6	55	54
7	28	27
K= 1, L= 6		
-6	-5	1
-5	37	-37
-4	59	62
-3	101	109
-2	12	-14
-1	99	-113
0	92	89
1	193	191
2	69	-70
3	181	-182
4	63	70
5	29	30
6	47	-46
K= 1, L= 7		
-6	34	-30
-5	15	7
-4	61	61
-3	12	2
-2	175	-207
-1	111	140
0	132	142
1	122	-109
2	121	-120
3	14	6
4	43	42
5	24	-28
K= 1, L= 8		
-5	105	92
-4	39	-38
-3	188	-216
-2	18	21
-1	115	143
0	30	-26
1	106	-102
2	71	71
3	54	56
4	104	-105
K= 1, L= 9		
-3	12	0
-2	67	85
-1	36	-42
0	71	-67
1	11	-4
2	33	35
3	39	39
K= 2, L= 0		
0	241	221
1	25	-10
2	127	-123
3	182	-170
4	168	192
5	22	18
6	-6	-10
7	111	111
8	15	11
K= 2, L= 1		
-8	39	-37
-7	-5	-3
-6	126	126
-5	16	-15
-4	544	-530
-3	59	-54
-2	964	1071
-1	849	909
0	26	33
1	839	-881
2	330	324
3	275	266
4	53	-62
5	117	-116
6	23	23
7	47	48
8	15	11
K= 2, L= 2		
-8	26	-24
-7	89	86
-6	29	33
-5	83	-79
-4	27	-24
-3	93	97
-2	86	-77
-1	16	14
0	190	-178
1	240	225
2	60	55
3	67	67
4	17	-18
5	118	-119
6	88	-91
7	40	43
8	17	9
K= 2, L= 3		
-8	49	45
-7	30	-31
-6	45	44
-5	32	32
-4	116	-114
-3	62	-63
-2	112	104
-1	16	18
0	253	-230
1	429	-406
2	118	-98
3	397	384
4	173	-203
5	201	-205
6	146	149
7	109	107
8	89	-91
K= 2, L= 4		
-7	29	-26
-6	27	29
-5	24	23
-4	209	-205
-3	42	-44
-2	288	296
-1	210	-223
0	167	-157
1	236	220
2	179	180
3	187	-185
4	149	-171
5	64	-67
6	144	150
7	75	70
K= 2, L= 5		
-7	47	42
-6	62	-59
-5	53	-53
-4	29	30
-3	53	60
-2	202	-214
-1	55	45
0	423	404
1	59	61
2	177	-178
3	89	-51
4	180	199
5	72	75
6	104	-108
7	75	-75
K= 2, L= 6		
-6	52	-46
-5	118	122
-4	108	110
-3	137	-165
-2	33	-37
-1	107	126
0	25	-25
1	26	26
2	21	-16
3	144	147
4	22	22
5	21	-20
6	27	-26
K= 2, L= 7		
-6	74	64
-5	20	-18
-4	-5	4
-3	9	8
-2	23	-27
-1	60	-73
0	17	19
1	86	94
2	87	-82
3	121	-117
4	115	122
5	18	18
K= 2, L= 8		
-5	33	28
-4	82	-78
-3	43	47
-2	23	-26
-1	77	-89
0	63	62
1	71	-69
2	68	-67
3	39	35
4	79	83
K= 2, L= 9		
-3	14	0
-2	99	119
-1	56	66
0	177	-124
1	118	-109
2	59	55
3	94	90
K= 3, L= 0		
1	403	390
2	61	66
3	224	-222
4	178	174
5	92	-87
6	66	-69
7	29	31
8	90	90
K= 3, L= 1		
-8	9	-1
-7	46	46
-6	131	131
-5	136	132
-4	293	-277
-3	437	-419
-2	33	-25
-1	896	942
0	146	126
1	499	-484
2	48	42
3	556	549
4	133	117
5	152	-148
6	56	-65
7	79	80
8	14	-2
K= 3, L= 2		
-8	23	-21
-7	55	-59
-6	53	52
-5	111	114
-4	162	158
-3	16	-10
-2	269	262
-1	211	-213
0	436	-403
1	14	12
2	400	389
3	36	37
4	183	-179
5	59	56
6	35	36
7	33	-37
8	45	-42
K= 3, L= 3		
-8	60	-54
-7	92	89
-6	83	84
-5	215	-221
-4	26	20
-3	341	333
-2	153	-146
-1	254	-248
0	86	77
1	42	32
2	141	127
3	316	-308
4	177	-164
5	137	-138
6	8	-6
7	106	-110
K= 3, L= 4		
-7	39	37
-6	56	-53
-5	31	-31
-4	56	58
-3	31	32
-2	320	-325
-1	71	-80
0	43	43
1	109	103
2	22	-22
3	67	66
4	16	-19
5	90	-90
6	-5	-3
7	-5	-3
K= 3, L= 5		
-7	33	-29
-6	13	-11
-5	25	25
-4	37	38
-3	27	-25
-2	108	-106
-1	47	-46
0	114	99
1	121	107
2	119	-119
3	166	-163
4	156	157
5	310	320
6	14	-12
7	133	-135
K= 3, L= 6		
-6	27	-23
-5	-5	4
-4	56	59
-3	90	102
-2	38	39
-1	144	-179
0	166	174
1	10	8
2	159	-151
3	26	29
4	115	120
5	52	49
6	27	-24
K= 3, L= 7		
-5	61	54
-4	135	137
-3	143	-147
-2	108	-120
-1	264	303
0	41	39
1	226	-222
2	34	-34
3	129	136
4	19	-18
5	135	-134
K= 3, L= 8		
-4	44	-42
-3	11	13
-2	14	10
-1	77	93
0	94	-90
1	62	-65
2	38	33
3	22	-17
4	36	-39
K= 3, L= 9		
-3	23	-15
-2	20	19
-1	21	19
0	34	29
1	57	-50
2	20	-13
3	-4	-1
K= 4, L= 0		
0	297	-275
1	119	-101
2	156	-143
3	461	453
4	10	7
5	195	-188
6	40	44
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K= 4, L= 1		
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3	40	-40
4	141	130
5	117	110
6	41	41
7	48	19
8	15	-13
K= 4, L= 2		
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-1	237	-232
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2	14	-11
3	46	-44
4	97	96
5	128	-127
6	15	13
7	98	105
8	38	-41
K= 4, L= 3		
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0	278	-256
1	121	125
2	107	116
3	102	-102
4	136	-142
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6	-5	5
7	18	1
K= 4, L= 4		
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2	170	-164
3	185	-182
4	23	26
5	147	149
6	-5	11
7	61	-69
K= 4, L= 5		
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1	90	-85
2	212	-211
3	207	-211
4	110	111
5	106	104
6	65	62
K= 4, L= 6		
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-4	113	-112
-3	-6	-2
-2	126	135
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0	74	-71
1	20	-17
2	155	147
3	76	74
4	77	-79
5	15	-17
6	36	-33
K= 4, L= 7		
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-3	61	-65
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0	110	-102
1	233	230
2	12	-7
3	40	-41
4	22	23
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K= 4, L= 8		
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1	103	-97
2	31	32
3	60	59
4	32	-29
K= 4, L= 9		
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0	153	-137
1	44	39
2	143	129
K= 5, L= 0		
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2	109	-101
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4	9	-7
5	66	-71
6	11	6
7	26	25
8	51	48
K= 5, L= 1		
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-2	-6	3
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1	120	-113
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3	47	52
4	141	-139
5	80	-84
6	156	164
7	84	86
8	29	-26
K= 5, L= 2		
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-6	40	41
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0	151	-156
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2	380	356
3	22	18
4	300	-287
5	70	74
6	158	160
7	83	-86
K= 5, L= 3		
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1	270	248
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3	154	-153
4	42	47
5	30	29
6	35	-39
7	15	-13
K= 5, L= 4		
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0	15	14
1	65	-67
2	34	-31
3	90	-91
4	105	-105
5	13	-12
6	41	39
7	27	-27
K= 5, L= 5		
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-4	105	-112
-3	27	-26
-2	13	-12
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1	298	295
2	23	-16
3	175	-174
4	-6	0
5	33	33
6	17	-14
K= 5, L= 6		
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-5	25	-24
-4	32	34
-3	-6	12
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0	174	174
1	373	-362
2	41	-38
3	404	412
4	167	172
5	162	-164
6	127	-126
K= 5, L= 7		
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-3	12	-5
-2	30	31
-1	28	-25
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1	122	-121
2	20	19
3	153	150
4	26	-26
5	53	-56
K= 5, L= 8		
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-2	42	40
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2	11	10
3	16	-12
4	43	-38
K= 5, L= 9		
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0	10	5
1	9	-15
2	59	-52
K= 6, L= 0		
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1	30	-22
2	131	130
3	103	103
4	231	-223
5	40	-38
6	37	38
7	9	4
K= 6, L= 1		
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-6	135	141
-5	225	-235
-4	73	-77
-3	43	37
-2	81	-80
-1	199	-183
0	154	-140
1	244	234
2	195	173
3	112	-108
4	23	-21
5	61	62
6	41	-40
7	45	48
K= 6, L= 2		
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-5	38	-41
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-3	129	125
-2	111	-110
-1	71	54
0	25	-20
1	401	-359
2	306	280
3	183	166
4	18	19
5	38	42
6	25	24
7	42	-45
K= 6, L= 3		
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-6	69	-66
-5	154	164
-4	79	88
-3	16	-18
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0	33	29
1	177	174
2	29	-26
3	123	-120
4	-6	9
5	60	60
6	-5	12
7	62	-65
K= 6, L= 4		
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-6	28	-26
-5	60	-61
-4	66	67
-3	-6	8
-2	103	-110
-1	90	-50
0	187	177
1	51	56
2	222	-216
3	-6	11
4	53	58
5	-5	14
6	117	-120
7	35	-36
K= 6, L= 5		
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-5	61	57
-4	73	81
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-2	46	-54
-1	101	101
0	32	-30
1	202	-196
2	67	-64
3	125	125
4	75	77
5	50	-49
6	-5	9
K= 6, L= 6		
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-5	51	48
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-3	87	-92
-2	178	191
-1	289	299
0	324	-328
1	267	-262
2	172	167
3	29	-32
4	83	77
5	90	90
K= 6, L= 7		
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-4	29	25
-3	41	41
-2	48	-51
-1	26	26
0	98	94
1	24	24
2	16	-12
3	23	20
4	37	-36
5	15	-14
K= 6, L= 8		
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-3	81	-77
-2	92	92
-1	53	57
0	53	-51
1	35	-32
2	83	80
3	49	45
K= 6, L= 9		
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0	10	-10
1	44	46
K= 7, L= 0		
1	173	-169
2	33	-30
3	-5	4
4	64	-65
5	49	-52
6	31	32
7	72	73
K= 7, L= 1		
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-6	-5	9
-5	27	29
-4	51	-49
-3	65	-70
-2	204	204
-1	94	-93
0	414	-387
1	105	101
2	85	88
3	107	-111
4	53	-56
5	32	-32
6	127	132
7	31	30
K= 7, L= 2		
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-6	75	76
-5	75	-74
-4	226	-238
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-2	273	267
-1	77	-77
0	273	-249
1	250	237
2	26	28
3	221	-223
4	18	20
5	204	224
6	57	60
7	77	-79
K= 7, L= 3		
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-6	98	-95
-5	88	90
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-3	61	-60
-2	252	-264
-1	17	16
0	494	464
1	47	43
2	173	-165
3	40	44
4	65	66
5	-5	5
6	27	-27
7	-4	-1
K= 7, L= 4		
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-5	107	107
-4	71	-73
-3	113	-126
-2	98	109
-1	71	73
0	25	-25
1	118	-117
2	75	73
3	53	-56
4	23	-24
5	45	45
6	18	-18
K= 7, L= 5		
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-5	-5	11
-4	26	-27
-3	31	31
-2	10	-7
-1	50	-56
0	138	141
1	34	32
2	377	-376
3	-6	0
4	135	133
5	68	-68
6	44	-42
K= 7, L= 6		
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-4	-6	-10
-3	77	-75
-2	23	-25
-1	102	107
0	93	94
1	37	32
2	222	-222
3	33	39
4	157	147
5	103	-107
K= 7, L= 7		
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-3	47	49
-2	24	26
-1	135	-134
0	73	-72
1	108	103
2	280	269
3	35	-31
4	121	-120
K= 7, L= 8		
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-2	34	-28
-1	90	-87
0	58	55
1	84	79
2	36	-34
3	65	-58
K= 8, L= 0		
0	99	-89
1	117	104
2	165	164
3	153	-152
4	248	-254
5	8	-4
6	73	74
7	22	-21
K= 8, L= 1		
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-6	104	-105
-5	159	-175
-4	138	147
-3	81	83
-2	244	-242
-1	142	-133
0	270	251
1	84	88
2	301	-274
3	24	21
4	36	-34
5	-5	7
6	18	21
7	21	-20
K= 8, L= 2		
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-6	20	-16
-5	139	-142
-4	110	122
-3	79	-80
-2	179	-184
-1	77	75
0	148	130
1	33	25
2	15	18
3	89	-91
4	9	0
5	58	68
6	64	65
7	18	19
K= 8, L= 3		
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-6	15	-14
-5	59	57
-4	90	94
-3	71	75
-2	191	-188
-1	126	-134
0	100	96
1	194	178
2	56	53
3	92	-85
4	108	108
5	34	29
6	66	-71
K= 8, L= 4		
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-5	-5	-6
-4	37	36
-3	44	57
-2	126	-136
-1	110	114
0	178	179
1	79	-76
2	141	-138
3	52	56
4	71	71
5	48	-49
6	88	-90
K= 8, L= 5		
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-5	82	76
-4	32	-31
-3	159	-166
-2	42	41
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0	14	-8
1	257	-253
2	154	157
3	172	178
4	267	-265
5	35	-36
6	61	63
K= 8, L= 6		
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-4	9	1
-3	-5	-2
-2	-5	5
-1	91	-96
0	66	-65
1	17	15
2	23	26
3	46	42
4	35	33
5	29	-30
K= 8, L= 7		
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-3	101	97
-2	33	-27
-1	42	-37
0	170	-160
1	-5	-15
2	144	135
3	51	51
4	36	-32
K= 8, L= 8		
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0	37	-37
1	22	19
2	38	39
K= 9, L= 0		
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2	160	155
3	21	-19
4	70	-68
5	-5	-1
6	25	-26
7	22	18
K= 9, L= 1		
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-6	39	-38
-5	176	179
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-3	167	-185
-2	242	258
-1	129	-128
0	247	-237
1	20	14
2	170	159
3	133	-134
4	119	-122
5	94	98
6	60	59
7	57	-56
K= 9, L= 2		
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-5	-5	-8
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-2	117	-121
-1	118	-113
0	17	19
1	136	125
2	196	-190
3	33	-33
4	126	132
5	-5	-2
6	19	-17
K= 9, L= 3		
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-4	134	136
-3	34	-30
-2	55	-64
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0	33	-30
1	89	-92
2	43	-44
3	149	165
4	100	113
5	13	-15
6	68	-72
K= 9, L= 4		
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-5	-5	1
-4	98	-99
-3	87	-84
-2	142	146
-1	94	102
0	50	-52
1	30	25
2	63	58
3	80	-86
4	92	98
5	20	18
6	72	-75
K= 9, L= 5		
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-4	21	-24
-3	90	90
-2	-5	1
-1	95	-107
0	-6	-3
1	34	29
2	10	-8
3	110	-102
4	91	93
5	49	45
K= 9, L= 6		
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-3	15	-15
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-1	27	28
0	163	-162
1	95	-91
2	-5	-5
3	86	82
4	101	-99
K= 9, L= 7		
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-1	86	-80
0	120	-115
1	95	93
2	75	69
3	57	-60
K= 9, L= 8		
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0	173	159
1	29	28
K= 10, L= 0		
0	175	173
1	209	205
2	143	-146
3	255	-262
4	76	79
5	93	92
6	39	41
K= 10, L= 1		
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-5	53	-52
-4	35	-34
-3	227	251
-2	160	-167
-1	126	-134
0	289	288
1	11	13
2	259	-253
3	86	-90
4	25	27
5	57	58
6	47	-46
K= 10, L= 2		
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-5	25	24
-4	12	-14
-3	98	-100
-2	72	77
-1	25	28
0	-6	-7
1	74	-65
2	64	-63
3	13	12
4	22	-20
5	64	68
6	-4	0
K= 10, L= 3		
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-5	85	-85
-4	8	-13
-3	44	42
-2	11	10
-1	77	-87
0	126	129
1	48	45
2	157	-171
3	24	-22
4	171	184
5	59	61
6	58	-56
K= 10, L= 4		
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-1	188	220
0	71	74
1	129	-125
2	35	-33
3	200	198
4	23	-28
5	193	-197
K= 10, L= 5		
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-4	57	-54
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-2	68	55
-1	58	71
0	68	-62
1	72	-71
2	55	56
3	28	25
4	63	-66
5	48	-45
K= 10, L= 6		
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-2	22	24
-1	57	-54
0	69	70
1	11	-11
2	-5	-5
3	27	-28
4	61	-59
K= 10, L= 7		
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-2	49	-45
-1	54	49
0	33	-27
1	50	-46
2	65	64
K= 11, L= 0		
1	198	201
2	161	163
3	152	-154
4	196	-204
5	25	26
6	93	94
K= 11, L= 1		
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-5	54	-57
-4	28	22
-3	-5	4
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0	86	86
1	24	24
2	26	26
3	130	-127
4	32	35
5	65	64
6	65	-65
K= 11, L= 2		
-6	63	-61
-5	42	39
-4	24	27
-3	41	-40
-2	101	-103
-1	-6	-17
0	129	136
1	86	-91
2	114	-121
3	-5	-1
4	71	73
5	-5	-1
6	38	-35
K= 11, L= 3		
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-4	28	-26
-3	97	-100
-2	23	-26
-1	99	104
0	50	-44
1	90	-85
2	40	40
3	61	58
4	53	-55
5	39	37
K= 11, L= 4		
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-4	33	-29
-3	-5	-13
-2	94	97
-1	70	-71
0	107	-121
1	131	139
2	136	145
3	10	-13
4	87	-86
5	28	24
K= 11, L= 5		
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-3	14	-14
-2	-5	9
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0	24	-30
1	31	-34
2	72	69
3	13	8
4	17	16
K= 11, L= 6		
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-1	18	-21
0	99	-99
1	13	12
2	94	96
3	34	-36
K= 11, L= 7		
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0	29	-27
1	71	67
K= 12, L= 0		
0	43	-39
1	447	454
2	51	49
3	122	-123
4	38	41
5	37	41
K= 12, L= 1		
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-2	47	-45
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0	26	-27
1	150	-157
2	65	-65
3	32	36
4	71	71
5	13	-16
K= 12, L= 2		
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-4	73	-76
-3	42	43
-2	52	53
-1	9	1
0	69	-69
1	19	-12
2	16	-19
3	44	-45
4	-5	2
5	-4	-2
K= 12, L= 3		
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-4	54	53
-3	-5	11
-2	30	-31
-1	31	-31
0	36	40
1	82	-81
2	41	-41
3	80	87
4	81	82
5	64	-66
K= 12, L= 4		
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-3	44	-43
-2	56	59
-1	28	17
0	20	-17
1	106	-111
2	27	25
3	181	187
4	10	4
K= 12, L= 5		
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-1	41	-36
0	59	-57
1	105	103
2	18	-18
3	50	-50
K= 12, L= 6		
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-1	12	-7
0	72	66
1	31	-31
2	57	-55
K= 13, L= 0		
1	50	-47
2	23	-23
3	87	85
4	39	-36
5	20	19
K= 13, L= 1		
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-4	-4	4
-3	97	-96
-2	27	23
-1	167	176
0	113	115
1	18	17
2	189	-188
3	53	-53
4	90	92
5	16	11
K= 13, L= 2		
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-2	43	-45
-1	100	102
0	58	59
1	139	-138
2	22	-25
3	100	103
4	33	33
K= 13, L= 3		
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-3	20	-20
-2	85	83
-1	55	57
0	158	-158
1	84	-90
2	114	119
3	-5	-2
4	69	-70
K= 13, L= 4		
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-2	44	-42
-1	-5	4
0	24	25
1	44	-47
2	22	20
3	55	54
K= 13, L= 5		
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-1	31	32
0	28	30
1	33	34
2	26	24
K= 13, L= 6		
0	37	-35
K= 14, L= 0		
0	162	154
1	45	-43
2	25	-24
3	50	53
4	11	-7
K= 14, L= 1		
-4	18	-14
-3	196	-204
-2	45	-45
-1	85	88
0	140	137
1	15	12
2	65	-63
3	35	35
4	58	52
K= 14, L= 2		
-4	31	-28
-3	81	82
-2	25	26
-1	34	-37
0	79	-82
1	-5	5
2	19	-18
3	15	11
4	46	47
K= 14, L= 3		
-3	46	-43
-2	11	-13
-1	29	29
0	10	-5
1	-5	1
2	68	-67
3	14	-15
K= 14, L= 4		
-2	22	21
-1	-3	-12
0	55	-54
1	16	15
2	95	99
K= 14, L= 5		
-1	119	-117
0	42	41
1	124	122
K= 15, L= 0		
1	23	-23
2	77	75
3	10	5
K= 15, L= 1		
-3	19	16
-2	108	-110
-1	22	-26
0	111	112
1	-4	0
2	110	-113
3	26	27
K= 15, L= 2		
-3	14	12
-2	116	123
-1	72	72
0	72	-73
1	101	-104
2	47	44
K= 15, L= 3		
-2	70	68
-1	94	-92
0	29	-27
1	45	44
2	35	36
K= 15, L= 4		
0	15	-15
K= 16, L= 0		
0	28	-26
1	61	-64
K= 16, L= 1		
-1	16	13
0	14	9
1	13	8
K= 16, L= 2		
0	33	-27

Table 5. *Least-squares planes**

Planes and deviations from plane (Å × 10^3)

	I	II	III
S	152	−168	**−4**
N(1)	**−1**	−201	
N(2)	242	**5**	
N(3)	162	**5**	**−4**
N(4)	787	75	**−4**
C(1)	**−4**	−397	
C(2)	**3**	−443	
C(3)	**−1**	109	
C(4)	**0**	189	
C(5)	**2**	−65	
C(6)	−10	**−5**	
C(7)	401	**−5**	**12**

Parameters of the plane†

	I	II	III
A (× 10^4)	9181	7957	7544
B (× 10^4)	3500	4930	5710
C (× 10^4)	−1858	−3518	−3237
D (Å)	3·831	4·567	5·030

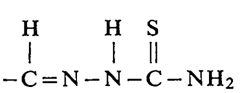
* Deviations in boldface type indicate atoms which were used to define the plane.

† Equation of the plane in the form:

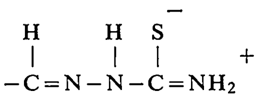
$$\text{deviation (Å)} = AX + BY + CZ + D\,,$$

with X, Y, Z the coordinates of the atom in Å relative to a, b, c^*.

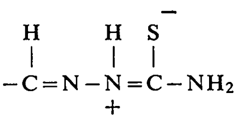
carbazones possesses only partial double-bond character in agreement with the canonical structures:



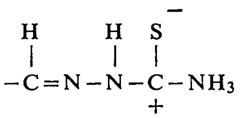
$$-\overset{H}{\overset{|}{C}}=N-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-NH_2$$



$$-\overset{H}{\overset{|}{C}}=N-\overset{H}{\overset{|}{N}}-\overset{\bar{S}}{\overset{|}{C}}=\overset{+}{N}H_2$$



$$-\overset{H}{\overset{|}{C}}=N-\underset{+}{\overset{H}{\overset{|}{N}}}=\overset{\bar{S}}{\overset{|}{C}}-NH_2$$



$$-\overset{H}{\overset{|}{C}}=N-\overset{H}{\overset{|}{N}}-\overset{\bar{S}}{\overset{|}{C}}-\underset{+}{NH_3}$$

The C(6)–N(2) bond should be a double bond in agreement with the value of 1·275 ± 0·003 Å found in our study. The corresponding C(7)–N(3) bond distance of 1·354 ± 0·003 Å and the C(7)–N(4) bond distance of 1·329 ± 0·003 Å are indicative of some double-bond character, in agreement with the above resonance firms.

A comparison of the N(2)–N(3) distance of 1·365 ± 0·003 Å with the corresponding N–N distance of 1·399 ± 0·006 Å in thiosemicarbazide reported by Domiano, Gasparri, Nardelli & Sgarabotto (1969) suggests that other canonical forms may be important. A similar shortening of the N–N bond to 1·372 Å in KTS was reported by Gabe *et al.* (1969) and to 1·374 Å in 2-formylthiophene thiosemicarbazone by Mathew & Palenik (1970). In contrast to the thiosemicarbazide, all three compounds have an extensively delocalized group attached to the nitrogen atom. The inclusion of resonance forms involving the pyridine ring in 4FPYTSC would account for the shortening of the N–N distance. This hypothesis is supported by the slight but not significant shortening of the C(5)–C(6), C(3)–C(4) and C(1)–C(2) bond lengths. The net result would be a slight negative charge on the pyridine ring nitrogen atom. Whether the increased negative charge is important in terms of biological activity is open to speculation. Structural studies currently in progress on other thiosemicarbazones may help explain some of the observed bond distances.

There are three hydrogen atoms bonded to nitrogen atoms which could form hydrogen bonds. The pertinent distances and angles involving these three hydrogen atoms are presented in Table 7. The two intermolecular hydrogen bonds which link the molecules are indicated in the molecular packing shown in Fig. 2. There are dimer-like molecules (similar to those found in carboxylic acids) formed by N–H···S hydrogen bonds across a center of symmetry. These N–H···S hydrogen bonds are weak since the N···S separation of 3·496 ± 0·002 Å is at the upper end of the range of values

Table 6. *Carbon–sulphur bond distances in related compounds*

Compound	C–S	Reference
4-Formylpyridine thiosemicarbazone	1·678 (2) Å	Present work
2-Formylthiophene thiosemicarbazone	1·698 (3) 1·691 (3)	Mathew & Palenik (1970)
2-Keto-3-ethoxybutyraldehyde bis(thiosemicarbazone)	1·692 (4) 1·687 (4) 1·689 (4) 1·682 (4)	Gabe *et al.* (1969)
Thiosemicarbazide	1·685 (5)	Domiano *et al.* (1969)
Ethionamide hydrochloride	1·69	Colleter & Gadret (1968)
α-Thiopyridone	1·68	Penfold (1953)
2*H*-Pyridaz-3-thione	1·698 (6)	Carlisle & Hossain (1966)

Table 7. *Hydrogen atom contacts*

D–*H*···*A*	Position of *A*	*D*–*H*	H···*A*	*D*···*A*	*D*–H···*A*
N(4)–H(24)···S	$1-x,\ 1-y,\ 1-z$	0·89 Å	2·63 Å	3·496 Å	164·1°
N(3)–H(23)···N(1)	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ -\frac{1}{2}-z$	0·88	2·13	2·961	159·0
N(4)–H(25)···N(2)	$x,\ y,\ z$	0·87	2·26	2·610	104·2

(3·2 to 3·5 Å) summarized by Srinivasan & Chacko (1967).

The dimer-like units are linked into a three-dimensional network by a strong N–H···N hydrogen bond. The N···N distance of 2·961 ± 0·003 Å is shorter than the majority of the $-NH_2$···ring–N distances reported by Fuller (1959), which average 3·06 ± 0·08 Å.

The second hydrogen atom, H(25), on the nitrogen atom N(2) forms no intermolecular hydrogen bonds, which may be a result of steric hindrance. Since the molecule is approximately planar and H(25) is oriented toward the pyridine ring, the approach of an acceptor atom is severely restricted. The H(25)···N(2) distance of 2·26 Å, which is less than a van der Waals contact, suggests a possible intramolecular hydrogen bond. However, both the N–H···N angle of 104·2° and the H–N···N angle of 57·1° argue against a hydrogen bond, leaving the question unresolved.

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References

CARLISLE, C. H. & HOSSAIN, M. B. (1966). *Acta Cryst.* **21**, 249.

COLLETER, J. C. & GADRET, M. (1968). *Acta Cryst.* B**24**, 513.

CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.

DOMIANO, P., GASPARRI, G. F., NARDELLI, M. & SGARABOTTO, P. (1969). *Acta Cryst.* B**25**, 343.

FRENCH, F. A. & BLANZ, E. J. JR (1966). *J. Med. Chem.* **9**, 585.

FULLER, W. (1959). *J. Phys. Chem.* **63**, 1705.

GABE, E. J., TAYLOR, M. R., GLUSKER, J. P., MINKIN, J. A. & PATTERSON, A. L. (1969). *Acta Cryst.* B**25**, 1620.

HAGENBACH, R. E. & GYSIN, H. (1952). *Experientia*, **8**, 184.

International Tables for X-ray Crystallography (1962). Vol. III, p. 211. Birmingham: Kynoch Press.

JONES, D. H., SLACK, R., SQUIRES, S. & WOOLDRIDGE, K. R. H. (1965). *J. Med. Chem.* **8**, 676.

MATHEW, M. & PALENIK, G. J. (1970). *Acta Cryst.* In the press.

PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 249.

PENFOLD, B. R. & WHITE, J. C. B. (1959). *Acta Cryst.* **12**, 130.

SRINIVASAN, R. & CHACKO, K. K. (1967). In *Conformation of Biopolymers*, Vol. 2, p. 607, New York: Academic Press.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement.* London: The Chemical Society.

Acta Cryst. (1970). B**26**, 1402

The Crystal and Molecular Structure of Dichloro-DL-methioninepalladium(II)

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Methionine and its metallic complexes have biological as well as chemical interest, because of their suspected antiviral and carcinostatic properties. The present palladium complex has been found to be a bidentate, and to form dimers in the crystalline state. It crystallizes in the monoclinic space-group $P2_1/n$ with four molecules per unit cell. Its cell parameters are $a = 6·920$, $b = 13·788$, $c = 10·531$ Å, $\beta = 94·69°$. Refinement of the structure was hampered by radiation damage and terminated at $R = 0·12$. Bond distances in the methionine portion of the molecule compare satisfactorily with those in the free methionine molecule.

Introduction

The structure of dichloro-DL-methioninepalladium(II), $PdCl_2(MtH)$, was originally investigated to discover the configuration of the ligand, in particular whether it was a bidentate or a tridentate. The sulphur and nitrogen atoms were expected to be bonded to the palladium atom, but the bonding of the oxygen atom was in doubt. Subsequent infrared studies by McAuliffe (1967) focused attention on the hydrogen bonding of the oxygen atoms and a preliminary report on this aspect has been published (Stephenson, McConnell & Warren, 1967).

There is general biological interest in this compound, since it is suspected that methionine, and its metal complexes to a greater extent, possess antiviral and carcinostatic properties. A comparison is made later between the structure of $PdCl_2(MtH)$ and the free methionine molecule (Mathieson, 1952).

Experimental

The crystals of $PdCl_2(MtH)$ were grown from aqueous solution in the form of fine needles, which were often twinned. The crystals broke easily on handling, so those chosen for X-ray study were mounted in Linde-