served between the oxygen atom and C(1). In the dimer, however, the oxygen of the aldehyde group is closest to the central carbon in the second half of the dimer molecule, C(10′), and the angle defined above is 85°30′ and the distance is 2·82 Å (Fig. 2).

The closest contacts to the oxygen atom at the equivalent point (000) are:

3·33 Å to C(8) at the equivalent point $(1\bar{1}0)$,
3·46 Å to C(2) at the equivalent point (001),
3·48 Å to C(7) at the equivalent point $(1\bar{1}0)$,

indicating that the molecules are held together by van der Waals forces only.

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A Refinement of the Crystal Structure of KSCN

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The crystal structure of KSCN has been redetermined in order to obtain more reliable bond distances for the thiocyanate ion. The C–S bond length was found to be 1·689 ± 0·013 Å, the C–N bond length 1·149 ± 0·014 Å, and the S–C–N angle 178·3 ± 1·2°.

Two previous investigations of the crystal structure of potassium thiocyanate have been made (Klug, 1933; Büssem, Günther & Tubin, 1934). Both studies made use of zonal data and differed substantially in only the position of the carbon atom in the thiocyanate ion. Because of the inherent errors in results from projection data and the growing need for more accurate interatomic distances for theoretical purposes, it was decided to reinvestigate this structure.

Crystals of analytical grade were recrystallized from an alcohol–water solution. Two separate crystals, whose dimensions varied from 0·07 to 0·10 mm, were used to collect the data because the first began to decompose before the investigation was complete. Systematic extinctions ($0kl$ for $k=2n+1$ and $h0l$ for $l=2n+1$) agree with the previous space group assignments of *Pbcm*. Lattice constants, determined from precession photographs, are $a=6{\cdot}673\pm0{\cdot}003$, $b=6{\cdot}715\pm0{\cdot}003$, $c=7{\cdot}543\pm0{\cdot}005$ Å. Intensity data were collected on a Picker diffractometer equipped with a General Electric single-crystal orienter using Mo $K\alpha$ radiation. Angle settings were calculated with an existing Fortran II program (Shoemaker, 1962). The Lorentz–polarization corrections were made but absorption effects were neglected. A three-dimensional Fourier synthesis (Sly, Shoemaker & Van den Hende, 1962), based on signs calculated from the positions of one of the previous investigations (Klug, 1933), gave the correct position for the carbon atom and improved the other positions. Anisotropic least-square refinement was carried out with the Busing, Martin & Levy (1962) program, and final values of $R_1=0{\cdot}080$ and $R_3=0{\cdot}067$ were obtained. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1962). Final parameters are listed in Table 1, with observed and calculated structure factors given in Table 2. The weighting scheme used is as follows:

$$\text{Weight}=1/\sigma^2$$
$$\sigma^2=F^2/4I^2[E+2B+(0{\cdot}1I)^2]$$

where F is the structure factor, I is the intensity, E is the total count and B is the background. Bond dis-

Table 1. *Final parameters and R values for* KSCN

Standard deviations are given in parentheses.
The β_{ij} are defined by: $T=\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$.
β_{13} and $\beta_{23}=0$ by symmetry.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
K	0·2059 (5)	0·25	0·0	0·0128 (8)	0·0089 (7)	0·0063 (5)	0·0
S	0·6033 (5)	0·1074 (5)	0·25	0·0085 (8)	0·0068 (9)	0·0068 (7)	−0·0008 (8)
C	0·7737 (19)	0·2919 (18)	0·25	0·0077 (32)	0·0132 (38)	0·0014 (21)	−0·0013 (31)
N	0·8934 (15)	0·4139 (16)	0·25	0·0094 (27)	0·0133 (31)	0·0061 (20)	0·0003 (30)

$$R_1=\sum_{hkl}\big||F_{\text{obs}}|-|F_{\text{calc}}|\big|/\sum_{hkl}|F_{\text{obs}}|=0{\cdot}080$$

$$R_3=\sqrt{\sum_{hkl}w(|F_{\text{obs}}|-|F_{\text{calc}}|)^2}\Big/\sqrt{\sum_{hkl}w(F_{\text{obs}})^2}=0{\cdot}067$$

tances and angles, calculated with the Busing, Martin & Levy (1964) function and error program, are given in Table 3.

The thiocyanate ion is found to be essentially linear (178·3 ± 1·2°) as expected. The S–C bond length is 1·69 ± 0·01 Å, considerably shorter than the single bond length of 1·81 Å. On the other hand the C–N bond length of 1·15 ± 0·01 Å is identical with the accepted triple bond length of 1·16 Å. This is quite similar to the trend found in KSeCN (Swank & Willett, 1965) in which the Se–C bond distance is 0·11 Å shorter than the single-bond distance but the C–N distance is again indicative of a triple bond. The bond distances observed here contrast sharply with those found in HNCS (Dousmanis, Sanders, Townes & Zeiger, 1953) and CH_3NCS (Beard & Dailey, 1949) where the group attached to the nitrogen allows only one π orbital on the nitrogen atom to enter into the π system. Thus the C–N distance increases to 1·21 Å and the C–S distance is shortened to 1·56 Å. A recent paper by Ferrari, Braibanti, Bigliardi & Lanfredi (1965) has summarized the S–C and C–N distances found in various thiocyanates. Four recent structures of first row transition metal thiocyanate complexes, $Ni[SC(NH_2)_2]_2(SCN)_2$ (Nardelli, Fava Gasparri, Giraldi Battistini & Domiano, 1966), $Zn(N_2H_4)_2(SCN)_2$ (Ferrari *et al.*, 1965), $Cu(en)_2(SCN)_2$ (Brown & Lingafelter, 1964) and $Ni(en)_2(SCN)_2$ (Brown & Lingafelter, 1963), give average S–C and C–N distances of 1·64 and 1·16 Å respectively. These distances are probably not significantly different from those of KSCN but the trend would indicate a slight weakening of the C–N bond and concurrent strengthening of the S–C bond which is consistent with the coordination of the thiocyanate group to the metal *via* the nitrogen end of the ion.

Table 2. *Observed and calculated structure factors for* KSCN

The columns contain h, $10|F_{obs}|$, and $10\,F_{calc}$. An unobserved reflection is denoted by a negative sign preceeding the value of $10|F_{obs}|$.

K= 0	L= 0	
1	144	-212
2	897	-942
3	664	-638
4	289	-269
5	953	997
6	408	-429
7	401	-326
K= 1	L= 0	
1	343	377
2	869	-865
3	946	980
4	403	376
5	-46	-51
6	170	-200
7	402	-429
K= 2	L= 0	
0	971	-1045
1	387	-369
2	1168	1129
3	683	686
4	614	-591
5	507	-530
6	-53	-79
K= 3	L= 0	
1	1211	1330
2	-38	29
3	342	322
4	633	-631
5	-51	-41
6	465	479
K= 4	L= 0	
0	141	144
1	603	583
2	810	-813
3	568	-602
4	676	695
5	98	114
6	253	278
K= 5	L= 0	
1	513	-575
2	97	-113
3	219	250
4	405	444
5	-58	-67
K= 6	L= 0	
0	861	-882
1	-52	9
2	295	292
3	227	241
4	97	114
K= 7	L= 0	
1	107	130
K= 1	L= 1	
1	152	162
2	969	-1012
3	400	366
4	299	-299
5	-47	-43
6	293	287
7	180	-181
K= 2	L= 1	
0	436	-427
1	923	979
2	306	-264
3	426	-370
4	409	392
5	546	-554
6	204	198
K= 3	L= 1	
1	65	-30
2	324	336
3	412	-343
4	-46	77
5	-51	66
6	82	-62
K= 4	L= 1	
0	223	-237
1	337	320
2	86	89
3	145	-101
4	-50	9
K= 5	L= 1	
1	343	-348
2	556	553
3	235	-230
4	281	299
5	-58	-33
K= 6	L= 1	
0	407	433
1	269	-282
2	-54	19
3	-56	83
K= 7	L= 1	
1	128	107
K= 0	L= 2	
0	958	-902
1	704	715
2	854	-907
3	683	-665
4	860	833
5	100	78
6	547	479
7	296	-272
K= 1	L= 2	
2	282	-274
3	270	213
4	789	806
5	155	-141
6	581	-600
K= 2	L= 2	
0	1034	-1148
1	241	-218
2	538	498
3	497	464
4	-45	12
5	439	-438
6	-55	4
K= 3	L= 2	
1	441	415
2	855	767
3	1179	-1162
4	343	-367
5	249	200
6	234	244
K= 4	L= 2	
0	1291	1273
1	165	-166
2	283	-313
3	249	-249
4	259	-237
5	623	650
K= 5	L= 2	
1	509	-531
2	417	-438
3	403	389
4	285	299
K= 6	L= 2	
0	-53	-94
1	232	-256
2	487	451
3	366	344
K= 1	L= 3	
1	143	-131
2	734	755
3	330	-305
4	246	255
5	83	38
6	265	-256
K= 2	L= 3	
0	356	324
1	674	-738
2	225	219
3	318	311
4	343	-349
5	575	483
6	192	-173
K= 3	L= 3	
1	68	39
2	286	-274
3	267	289
4	-50	-75
5	-54	-61
6	84	58
K= 4	L= 3	
0	225	226
1	212	-264
2	113	-90
3	78	78
4	-53	-1
5	269	288
K= 5	L= 3	
1	273	294
2	459	-495
3	199	214
4	244	-259
K= 6	L= 3	
0	375	-408
1	206	245
2	-56	2
3	-58	-62
K= 0	L= 4	
0	2290	2018
2	601	-611
4	157	-180
6	320	-347
K= 1	L= 4	
1	260	-267
2	568	-570
3	652	672
4	262	279
5	-53	-37
6	237	-166
K= 2	L= 4	
0	659	-690
1	247	-247
2	719	761
3	507	501
4	507	-450
5	398	-432
6	-58	-57
K= 3	L= 4	
1	825	914
2	-46	8
3	204	229
4	530	-497
5	40	-36
K= 4	L= 4	
0	-48	121
1	403	442
2	594	-624
3	443	-475
4	522	557
K= 5	L= 4	
1	387	-457
2	86	-95
3	143	207
K= 6	L= 4	
0	792	-718
1	-57	-0
K= 1	L= 5	
1	84	93
2	471	-522
3	242	244
4	-174	-190
5	-56	-33
K= 2	L= 5	
0	275	-260
1	571	505
2	157	-153
3	218	-224
4	264	272
5	377	-386
K= 3	L= 5	
1	-48	-7
2	178	218
3	213	-239
4	-55	42
K= 4	L= 5	
0	154	-159
1	189	206
2	-53	56
3	-55	-72
4	-58	-3
K= 5	L= 5	
1	228	-266
2	312	375
K= 0	L= 6	
0	190	-164
1	361	356
2	444	-462
3	368	-382
4	517	482
K= 1	L= 6	
1	909	-882
2	137	-138
3	165	144
4	450	511
K= 2	L= 6	
0	518	-578
1	-50	-107
2	291	282
3	258	274
4	-57	8
K= 3	L= 6	
1	257	262
2	420	468
3	784	-720
K= 4	L= 6	
0	787	764
1	85	-97
2	193	-204
K= 1	L= 7	
1	-53	-72
2	285	352
3	152	-168
K= 2	L= 7	
0	169	158
1	351	-350
2	107	127
3	138	171
K= 3	L= 7	
1	-57	14
2	114	-145
K= 0	L= 8	
0	925	921
1	-58	-18
K= 1	L= 8	
1	168	-133

Table 3. *Bond lengths and angles*

The number following the atom signifies the following symmetry transformation of coordinates given in Table 1.

0 x, y, z
1 $1-x, y, z$
2 $1-x, 1-y, \frac{1}{2}+z$

	This work	Klug	Bussen
C(0)–N(0)	1·149 (14)	1·15	1·16
S(0) –C(0)	1·689 (13)	1·79	2·12
K(0)–N(1)	2·974 (9)		
K(0)–N(2)	2·982 (8)		
K(0)–S(0)	3·364 (4)		
K(0)–S(1)	3·272 (3)		
S(0) –C(0)–N(0)	178·3° (1·2)	180°	129·1°

The packing of the molecules is essentially the same as described before by Klug (1933). The potassium ion is at the center of a distorted square antiprism with four sulfur atoms, two at 3·36 and two at 3·27, and four nitrogen atoms, two at 2·97 and two at 2·98, occupying the vertices. The sums of the ionic radii are 3·17 and 3·04 respectively for K–S and K–N and thus the observed distances are quite reasonable.

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