The Crystal Structure of Thallium(I) Diisobutyldithiocarbamate

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The crystal structure of thallium(I) diisobutyl-dithiocarbamate, $Tl(I)S_2CN(C_4H_9)_2$, has been determined from three-dimensional X-ray data. The crystals are triclinic, space group $P\bar{1}$. Unit cell parameters:

$a = 7.866(2)$ Å, $b = 13.945(3)$ Å, $c = 6.218(2)$ Å, $\alpha = 89.27(1)°$, $\beta = 93.06(1)°$, $\gamma = 103.29(2)°$.

There are two formula units per elementary cell. The structure may be regarded as consisting of dimers with the composition $[TlS_2CN(C_4H_9)_2]_2$ linked by thallium-sulfur coordination in linear strings in the c direction. The thallium-sulfur coordination is five-fold. The metal-metal distance within the dimer is 3.678(2) Å, whereas the shortest distance between metal atoms in different dimers is 5.193(2) Å. The metal atom arrangement thus consists of distinct pairs. The dimeric unit is rather similar to that of thallium diisopropyldithiocarbamate, but the orientation of the dimers in the strings and the metal atom arrangement are quite different. The difference between the structures is discussed with respect to the space requirement of the alkyl ligands.

The structures of several thallium(I) dialkyldithiocarbamates have been determined by the present research group.[1-5] All of these compounds may be considered as built from dimeric molecules linked by thallium-sulfur coordination. The nature of the linkage is, however, rather different, apparently depending on the length of the alkyl ligands. The resulting metal atom arrangement changes from a two-dimensional network of metal atoms in the methyl compound to chains in the two propyl compounds. The coordination numbers also decrease in the series. Since it could be expected that this process would continue with still larger ligands the present compound has been investigated.

UNIT CELL AND SYMMETRY

Formula unit: $Tl(I)S_2CN(C_4H_9)_2$
Crystal system: triclinic
Unit cell parameters:
$a = 7.866 \pm 0.002$ Å, $b = 13.945 \pm 0.003$ Å,
$c = 6.218 \pm 0.002$ Å, $\alpha = 89.27 \pm 0.01°$
$\beta = 93.06 \pm 0.01°$ $\quad \gamma = 103.29 \pm 0.02°$
Volume of unit cell: 662.8 Å³
Density (measured): 2.034 g cm⁻³
Number of formula units per unit cell: 2
Density (calculated): 2.049 g cm⁻³
Space group: $P\bar{1}$

EXPERIMENTAL

Crystals of thallium(I) diisobutyldithiocarbamate were prepared according to the method published by Åkerström.[6] They were crystallized from acetone and benzene (1:1) as long pale yellow needles with the needle axis parallel to the c axis. Their density was determined by the flotation method using an aqueous solution of K_2HgI_4. The unit cell dimensions were determined from a Guinier-Hägg powder photograph taken with $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å) with silicon ($a = 5.4305$ Å)[7] as internal standard.

For the intensity data, $CuK\alpha$ radiation was used. The X-ray reflections were recorded on equi-inclination Weissenberg photographs using the multiple film technique (five films). With the crystal rotating about the needle axis the layers $0 \leq l \leq 4$ were recorded. The crystals were found to decompose slowly in the X-ray beam, and for that reason four crystals were used for the exposures. Details of the crystals are given in Table 1. In all 1409 independent reflections were recorded.

The relative intensities of the reflections were measured with an automatic film scanner SAAB AFS MK II,[8,9] connected on-line to an IBM 1800 processor controller at this Institute. They were corrected for Lorentz and polarisation effects but not for absorption and extinction.

Table 1. Crystals used for the exposures.

Crystal	Dimensions in mm			Layers recorded	Number of reflections
1	0.038	0.045	0.150	$hk0$, $hk1$	547
2	0.050	0.060	0.154	$hk2$, $hk3$	613
3	0.038	0.033	0.108	$hk4$	222
4	0.020	0.028	0.108	interlayer scaling	81

The usual orientation of the film, with the central line parallel to the scanning direction, allows an interval of 185° to be measured. In order to obtain sufficient overlap for the scaling of the two halves of each layer from the triclinic crystal it was necessary to increase the scanning area. By scanning the film with the central line normal to the scanning direction, *i.e.* parallel to the drum axis, it was possible to measure the entire recorded area, corresponding to a crystal rotation of 220°. The indexing was then performed by hand. For the calculation of the integrated intensities the computer programs written by Werner [9] were used. The parameters for the integration procedure were the same as those used in a previous determination at this Institute.[1] A correction factor (FK = 0.5) for the intensities of the strong reflections was applied as suggested by Werner [10] from a study of film factors. The area of integration for each reflection was large enough to include both the α_1 and the α_2 component. The film factors were initially calculated using standard methods, but they differed somewhat from those usually

obtained. After the determination of the atomic positions the film factors were therefore systematically varied as will be described later.

Interlayer scale factors were obtained by exposing reflections from all the layers on the same film set. Only small changes in these values were noticed when the individual scale factors were included in the final refinement.

DETERMINATION OF THE ATOMIC POSITIONS

The approximate positions of the thallium and sulfur atoms were found from three-dimensional Patterson syntheses. The coordinates of these atoms were refined by the method of least squares. The nitrogen and carbon atoms were located in a three-dimensional difference synthesis. No attempt was made to locate the hydrogen atoms.

Table 2. Atomic coordinates and thermal parameters, listed as isotropic B or anisotropic b_{ij}. The anisotropic temperature factor is defined as $\exp(-b_{11}hh - 2b_{12}hk \cdots)$. The standard deviation corresponding to the last digit is shown in parentheses.

Atom	x	y	z	B (Å^2)
Tl	0.1897(1)	−0.01149(7)	−0.1499(2)	
S_1	0.1014(7)	0.1834(4)	−0.0441(10)	
S_2	0.1790(8)	0.0604(4)	0.3218(11)	
C_0	0.2099(23)	0.1742(13)	0.1995(37)	2.2(3)
N	0.3237(19)	0.2525(11)	0.2865(30)	2.2(3)
C_{11}	0.3479(26)	0.3505(14)	0.1868(37)	3.9(4)
C_{21}	0.4292(26)	0.2436(15)	0.4870(40)	2.8(4)
C_{12}	0.2078(28)	0.4047(16)	0.2418(43)	3.2(4)
C_{22}	0.5925(27)	0.2042(15)	0.4434(41)	2.9(4)
C_{13}	0.2381(38)	0.5037(21)	0.1312(52)	4.8(6)
C_{23}	0.6876(47)	0.1914(27)	0.6606(65)	6.8(8)
C_{14}	0.2000(37)	0.4176(21)	0.4891(53)	5.0(6)
C_{24}	0.7136(35)	0.2728(20)	0.2888(51)	4.6(6)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Tl	0.0140(2)	0.00370(5)	0.0135(37)	0.00071(5)	0.0009(1)	−0.0015(1)
S_1	0.0171(10)	0.0068(3)	0.0068(43)	−0.0004(4)	−0.0047(11)	−0.0001(5)
S_2	0.0208(12)	0.0025(2)	0.0084(44)	−0.0018(4)	−0.0075(11)	−0.00002(50)

Table 3. Observed and calculated structure amplitudes. Reflections marked with an asterisk were not included in the refinement.

The coordinates and isotropic temperature factors of all but the hydrogen atoms were refined by the method of least squares using a full matrix program. In the expression minimized, $\sum\omega(|F_o|-|F_c|)^2$, the weights, ω, were calculated according to the equation suggested by Cruickshank *et al.*[11] $\omega=1/(a+|F_o|+c|F_c|^2+d|F_o|^3)$. The constants used were $a=40.0$, $c=0.0154$, $d=0.0$. Atomic scattering factors for the neutral elements obtained from Hanson *et al.*[12]

were used with addition of the real part of the dispersion correction.[13] The discrepancy index $R=\sum|(|F_o|-|F_c|)|/\sum|F_o|$, was then 0.114. The nine scale factors and the anisotropic temperature factors for the thallium and sulfur atoms were then included in the refinement. The imaginary part of the dispersion correction for thallium was then applied.[13] The least-squares calculations were continued until the shifts on the parameters were less than one percent of

Table 3. Continued.

4	-4	850	868
4	-3	683	751
4	-2	535	592
4	-1	658	753
4	0	793	930
4	1	883	1022
4	2	866	1002
4	3	698	763
4	4	490	526
4	5	538	547
4	6	524	618
4	7	529	559
4	8	341	306
4	11	178	182
5	-9	206	217
5	-6	245	217
5	-5	243	217
5	-4	217	200
5	-3	300	259
5	-2	394	408
5	-1	431	399
5	0	530	579
5	1	642	662
5	2	516	526
5	3	267	290
5	4	397	396
5	5	433	492
5	6	419	489
5	7	351	336
5	8	216	249
5	9	244	246
5	10	272	315
6	-13	287	291
6	-12	263	265
6	-11	285	292
6	-10	377	392
6	-9	428	407
6	-8	406	377
6	-7	465	438
6	-6	303	281
6	-5	204	220
6	-4	341	291
6	-3	458	422
6	-1	203	184
6	1	304	256
6	2	403	387
6	3	329	322
7	-8	228	235
7	-6	204	194
7	-5	321	307
7	-3	417	406
7	-2	373	367
7	-1	361	319
7	0	513	478
7	1	582	519
7	2	480	479
7	3	418	408
7	4	339	376
7	5	297	319
7	6	270	292
9	-3	255	188
	H,K,3		
-9	0	217	142
-8	-2	208	217
-8	-1	275	284
-8	0	349	330
-8	1	257	281
-8	2	228	264
-8	3	332	321
-8	4	305	296
-8	5	296	325
-8	6	303	318
-8	7	364	343
-8	8	188	236
-8	9	201	207
-7	-4	170	182
-7	4	236	252
-7	5	342	318
-7	6	240	247
-7	7	232	193
-7	9	265	280
-7	10	235	291
-7	11	223	244
-6	-8	238	275
-6	-7	252	318
-6	-6	385	403
-6	-5	522	509
-6	-4	464	440
-6	-3	446	425
-6	-2	401	410
-6	-1	411	378
-6	0	475	400
-6	1	403	391
-6	2	446	404
-6	3	444	419
-6	4	229	170
-6	5	260	252
-6	6	335	316
-6	7	375	350
-5	-6	261	238
-5	-5	283	307
-5	-4	371	331
-5	-3	329	334
-5	-2	194	198
-5	-1	335	313
-5	0	578	587
-5	1	636	650
-5	2	569	551
-5	3	375	354
-5	4	533	562
-5	5	798	824
-5	6	657	679
-5	7	665	621
-5	8	508	504
-5	9	468	489
-5	10	468	485
-5	11	428	442
-5	12	442	426
-5	13	266	304
-5	14	186	214
-4	-10	217	236
-4	-9	359	333
-4	-8	347	349
-4	-7	461	442
-4	-6	398	359
-4	-5	339	332
-4	-4	444	425
-4	-3	537	518
-4	-2	428	392
-4	-1	207	205
-4	4	224	196
-4	6	283	251
-4	7	247	242
-4	8	329	126*
-4	10	196	184
-4	12	331	289
-3	-10	370	370
-3	-9	528	509
-3	-8	603	615
-3	-7	664	664
-3	-6	525	542
-3	-5	672	717
-3	-4	822	847
-3	-3	889	911
-3	-2	738	784
-3	-1	624	632
-3	0	684	737
-3	1	786	841
-3	2	812	843
-3	3	729	761
-3	4	694	713
-3	5	733	698
-3	6	545	553
-3	7	824	810
-3	8	711	725
-3	9	528	497
-3	10	357	360
-3	11	325	304
-3	12	392	405
-3	13	325	281
-2	-5	159	119
-2	-3	174	176
-2	-2	224	212
-2	-1	192	147
-2	0	349	318
-2	1	397	392
-2	2	764	807
-2	3	647	691
-2	4	673	686
-2	5	650	630
-2	6	861	887
-2	7	869	895
-2	8	719	734
-2	9	725	680
-2	10	595	550
-2	11	501	486
-2	12	537	519
-2	13	518	400
-2	14	400	384
-2	15	189	249
-1	-13	225	290
-1	-12	374	376
-1	-11	425	418
-1	-10	365	394
-1	-9	449	436
-1	-8	664	618
-1	-7	957	893
-1	-6	826	874
-1	-5	888	912
-1	-4	679	699
-1	-3	785	797
-1	-2	1015	1006
-1	-1	756	813
-1	0	682	687
-1	1	451	468
-1	2	211	206
-1	3	432	389
-1	4	342	337
-1	5	325	306
-1	13	194	74*
0	-15	293	93*
0	-12	293	228
0	-10	233	203
0	-9	527	452
0	-8	721	700
0	-7	681	661
0	-6	742	705
0	-5	669	675
0	-4	624	643
0	-3	887	845
0	-2	959	996
0	-1	743	918
0	1	371	485
0	2	929	992
0	3	1023	1048
0	4	1053	1034
0	5	939	960
0	6	862	874
0	7	857	838
0	8	827	856
0	9	917	869
0	10	753	749
0	11	510	507
0	12	421	406
0	13	376	309
0	14	321	352
1	-15	165	237
1	-11	324	295
1	-10	254	271
1	-9	264	276
1	-6	330	328
1	-5	634	640
1	-4	455	434
1	-3	174	151
1	0	389	344
1	1	180	168
1	2	463	416
1	3	513	482
1	4	647	635
1	5	399	359
1	6	436	393
1	7	575	551
1	8	610	610
1	9	579	588
1	10	424	411
1	12	228	240
1	13	316	311
1	14	289	336
2	-12	387	382
2	-11	445	428
2	-10	501	491
2	-9	462	459
2	-8	550	545
2	-7	910	843
2	-6	1078	1121
2	-5	995	1048
2	-4	745	797
2	-3	688	737
2	-2	970	1018
2	-1	1041	1079
2	0	934	918
2	1	545	499
2	2	656	640
2	3	488	460
2	4	488	440
2	5	628	605
2	6	590	538
2	7	408	388
2	8	239	239
2	9	303	265
2	10	450	445
2	11	363	344
2	12	201	205
3	-8	267	260
3	-7	523	468
3	-6	527	462
3	-5	338	299
3	-4	266	254
3	-3	252	285
3	-2	443	427
3	-1	574	573
3	0	652	652
3	1	450	424
3	2	343	335
3	3	463	448
3	4	977	953
3	5	899	889
3	6	670	669
3	7	553	550
3	8	566	572
3	9	682	735
3	10	670	677
3	11	431	475
3	12	314	333
4	-12	234	204
4	-11	270	328
4	-10	429	424
4	-9	296	311
4	-8	245	281
4	-7	406	399
4	-6	488	468
4	-5	593	570
4	-4	637	610
4	-3	467	466
4	-2	397	407
4	-1	310	278
4	0	346	361
4	1	386	341
4	2	201	220
4	4	245	203
4	8	208	170
4	9	200	219
5	-11	219	241
5	-10	313	316
5	-9	405	325
5	-8	446	424
5	-7	399	385
5	-6	529	512
5	-5	763	696
5	-4	727	708
5	-3	512	540
5	-2	401	409
5	-1	523	484
5	0	714	731
5	1	616	574
5	2	395	390
5	3	274	290
5	4	416	409
5	5	448	440
5	6	502	478
5	7	453	453
5	8	319	325
5	9	245	272
6	4	254	250
6	5	334	349
6	6	383	398
6	7	318	339
6	9	315	279
7	-9	200	256
7	-8	333	322
7	-7	271	284
7	-6	257	299
7	-5	277	318
7	-4	360	371
7	-3	438	419
7	-2	367	364
7	-1	243	255
7	0	235	252
7	2	310	245
7	3	220	186
7	4	210	70*
8	-4	193	241
8	-1	180	199
8	1	208	224
8	2	194	256
	H,K,4		
-8	-1	202	250
-8	0	211	227
-7	-2	250	267
-7	-1	360	359
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-7	1	320	357
-7	2	345	303
-7	3	348	327
-7	4	426	419
-7	5	383	377
-7	6	272	330
-7	8	244	304
-7	10	234	278
-7	11	182	269
-5	-8	250	262
-5	-6	344	324
-5	-5	418	398
-5	-4	508	495
-5	-3	439	420
-5	-2	462	430
-5	-1	593	587
-5	0	591	581
-5	1	606	600
-5	2	555	555
-5	3	501	511
-5	4	581	542
-5	5	351	361
-5	6	439	417
-5	7	368	399
-4	-4	293	299
-4	-3	347	253
-4	-2	385	368
-4	-1	433	373
-4	0	527	529
-4	1	610	612
-4	2	478	471
-4	3	487	466
-4	4	437	471
-4	5	528	511
-4	6	640	621
-4	7	412	429
-4	8	465	431
-4	9	399	414
-4	10	469	476
-4	11	462	474
-4	12	369	398
-4	13	290	344
-4	14	265	324
-3	-12	231	289
-3	-11	289	303
-3	-10	296	332
-3	-9	400	398
-3	-8	538	504
-3	-7	350	362
-3	-6	340	290
-3	-5	294	283
-3	-4	380	375
-3	-3	445	448
-3	-2	436	375
-3	-1	367	363
-3	0	303	281
-3	1	333	322
-3	2	408	378
-3	3	387	355
-3	4	397	364
-3	12	255	217
-2	-9	363	364
-2	-8	369	357
-2	-7	267	261
-2	-6	370	373
-2	-5	379	345
-2	-4	723	671
-2	-3	858	828
-2	-2	823	876
-2	-1	773	749
-2	0	723	753
-2	1	878	973
-2	2	1076	1093
-2	3	1054	1021
-2	4	805	806
-2	5	634	596
-2	6	719	704
-2	7	614	593
-2	8	706	655
-2	9	453	444
-2	10	301	288
-2	11	275	307
-2	13	283	320
-1	-13	225	293
-1	-12	297	328
-1	-11	334	279
-1	-8	304	325
-1	-7	264	256
-1	-6	244	208
-1	-4	298	237
-1	-3	208	163
-1	-2	259	197
-1	-1	143	108
-1	0	223	232
-1	1	508	538
-1	2	502	476
-1	3	392	344
-1	5	372	345
-1	6	466	393
-1	7	479	443
-1	8	509	484
-1	9	360	376
-1	10	424	386
-1	11	420	397
-1	12	453	472
-1	13	504	540
-1	14	312	391
0	-14	262	322
0	-13	365	414
0	-12	469	438
0	-11	427	432
0	-10	470	401
0	-9	416	406
0	-8	533	528
0	-7	644	654
0	-6	745	739
0	-5	299	294
0	-4	423	369
0	-3	668	646
0	-2	907	925
0	-1	873	904
0	1	500	568
0	2	709	757
0	3	788	757
0	4	979	860
0	5	625	583
0	6	437	366
0	8	314	261
0	9	356	279
1	-8	282	275
1	-7	269	229
1	-4	658	597
1	-3	738	658
1	-2	863	817
1	-1	703	754
1	0	714	724
1	1	909	922
1	2	864	855
1	3	1014	1013
1	4	940	907
1	5	704	663
1	6	511	516
1	7	529	501
1	8	658	630
1	9	605	572
1	10	443	419
1	12	289	302
1	13	375	403
2	-13	233	262
2	-12	328	387
2	-11	491	494
2	-10	460	465
2	-8	382	338
2	-7	425	385
2	-6	492	502
2	-5	287	291
2	-4	225	194
2	0	246	221
2	3	302	287
2	5	265	221
2	12	223	299
3	-13	256	291
3	-12	298	364
3	-11	349	356
3	-9	425	335
3	-8	402	412
3	-7	425	408
3	-6	499	496
3	-5	477	488
3	-4	467	478
3	-3	434	417
3	-2	643	681
3	-1	787	873
3	0	761	781
3	1	668	702
3	2	593	610
3	3	859	813
3	4	779	796
3	5	580	610
3	6	547	547
3	7	358	349
4	-3	270	212
4	-2	470	437
4	-1	490	499
4	0	382	429
4	1	344	370
4	2	453	372
4	3	543	545
4	4	413	459
4	5	460	461
4	6	316	286
4	8	248	272
4	9	287	339
4	10	312	359
5	-11	328	348
5	-10	338	376
5	-9	380	397
5	-8	383	328
5	-6	363	357
5	-5	332	348
5	-4	346	328
5	1	400	300
5	4	288	164
5	6	273	268
6	-5	260	271
6	-4	262	338
6	-1	376	383
6	0	490	486
6	1	626	562
6	2	417	428
6	3	353	384
6	4	314	368
6	5	423	438
6	6	338	388

the estimated standard deviations. At this stage of the refinement the discrepancy index R was 0.087.

As mentioned above the film factors seemed to be somewhat lower than those usually observed, *e.g.* 2.3 for the zero layer. The errors appeared to be associated with a systematic underestimation of the intensities of the strong reflections. New sets of observed intensities were calculated using the film factors 2.5, 2.7, 2.9, 3.1 for the zero layer. The film factors for the layers $l = 1,2,3$ were determined by interpolation between the selected value for $l = 0$ and the film factor for $l = 4$ which was held constant at the observed value 3.25. For each of these sets of intensities three additional cycles of refinement were run. The R value decreased continuously to 0.063 for the zero-layer film factor 3.1 but was only sligthly higher, 0.065, for the film factor 2.9. The film factor 2.9 which agrees well with the published value 2.93 for the film used,[14] Ilford Industrial G, was then selected as the final value. Changes in the atomic coordinates were negligible.

The final atomic and thermal parameters are shown in Table 2. The observed and calculated structure amplitudes are listed in Table 3 and the interatomic distances and angles in Table 4.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General features. The structure consists of centrosymmetric dimeric molecules $[\mathrm{TlS_2CN(C_4H_9)_2}]_2$. There is one such molecule in the unit cell. The molecule is shown in Fig. 1 which also shows the notation of the atoms. The arrangement of the molecules is illustrated in Fig. 2.

Table 4. Distances and angles. The notation used is shown in Fig. 1. Atoms which have been transformed according to the centrosymmetry are denoted by a bar. An asterisk represents the translation $-c$.

(a) Metal-metal distance

Atoms	Distance(Å)
$Tl-\overline{Tl}$	3.678(2)

(b) Distances and angles of coordination.

Atoms	Distance(Å)	Atoms	Angle(°)	Atoms	Angle(°)
$Tl-S_1$	3.043(5)	$S_1-Tl-\overline{S}_1$	107.6(1)	$S_2-Tl-\overline{S}_2$	105.7(2)
$Tl-\overline{S}_1$	3.184(5)	S_1-Tl-S_2	57.2(2)	$\overline{S}_1-Tl-\overline{S}_2$	57.3(2)
$Tl-S_2$	3.123(6)	$\overline{S}_1-Tl-S_2$	77.8(2)	$S_1-Tl-\overline{S}_2$	82.5(2)
$Tl-\overline{S}_2$	2.966(6)	S_1-Tl-S_2*	86.6(2)	$\overline{S}_1-Tl-S_2*$	123.2(2)
$Tl-S_2*$	3.424(7)	S_2-Tl-S_2*	143.5(2)	$\overline{S}_2-Tl-S_2*$	71.5(2)

(c) Distances and angles in the dithiocarbamate ligand

Atoms	Distance(Å)	Atoms	Angle(°)	Atoms	Angle(°)
S_1-C_0	1.72(2)	$Tl-S_1-C_0$	85.4(6)	$Tl-\overline{S}_1-C_0$	83.0(6)
S_2-C_0	1.72(2)	$Tl-S_2-C_0$	82.8(8)	$Tl-\overline{S}_2-C_0$	89.9(7)
C_0-N	1.34(2)	$S_1-C_0-S_2$	118(1)	S_1-C_0-N	121(2)
$N-C_{11}$	1.47(3)	S_2-C_0-N	121(2)	C_0-N-C_{11}	121(2)
$N-C_{21}$	1.48(3)	C_0-N-C_{21}	121(2)	$C_{11}-N-C_{21}$	117(2)
$C_{11}-C_{12}$	1.53(3)	$N-C_{11}-C_{12}$	113(2)	$N-C_{21}-C_{22}$	112(2)
$C_{12}-C_{13}$	1.51(4)	$C_{11}-C_{12}-C_{13}$	111(2)	$C_{11}-C_{12}-C_{14}$	112(2)
$C_{12}-C_{14}$	1.56(4)	$C_{13}-C_{12}-C_{14}$	110(2)		
$C_{21}-C_{22}$	1.55(3)	$C_{21}-C_{22}-C_{23}$	108(2)	$C_{21}-C_{22}-C_{24}$	112(2)
$C_{22}-C_{23}$	1.54(5)	$C_{23}-C_{22}-C_{24}$	112(2)		
$C_{22}-C_{24}$	1.55(4)				

(d) Intermolecular distances less than 4.0 Å. The relation of the second atom to the coordinates x,y,z of Table 2 is shown.

Atoms		Distance (Å)
Tl	$S_2(x,y,z-1)$	3.424
S_1	$C_{23}\ (x-1,y,z-1)$	3.674
S_2	$S_2\ (-x,-y,1-z)$	3.750
S_2	$C_{23}\ (1-x,-y,1-z)$	3.887
C_{12}	$C_{24}\ (x-1,y,z)$	3.924
C_{11}	$C_{11}\ (x,y,z-1)$	3.950
C_{13}	$C_{13}\ (-x,1-y,-z)$	3.984

It follows from the triclinic space group that all of the molecules are parallel. The central parts of the molecules are located close to the ca plane. The bulky organic ligands project from both sides of this plane to completely exclude any other interaction than van der Waals forces between dimers in different planes. In these planes the dimers are linked together by metal-sulfur interaction to form linear strings running in the c direction.

The dimer. The distances and angles in the dimeric unit are presented in Table 4. The two formula units are related by a centre of symmetry. The thallium and sulfur atoms in the central part of the dimer can be described as a bipyramid with a sulfur parallelogram as the common basis. This parallelogram has nearly rectangular shape; the corner angles are 87.9 and 92.1°, and the length of the edges 3.96 and 2.95 Å. The shorter edge corresponds to the sulfur-sulfur distances within the dithiocarbamate ligand. The distances from each metal
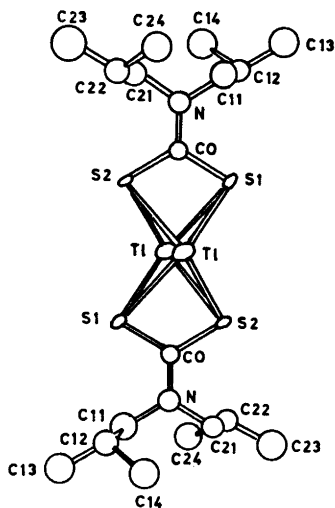
Fig. 1. The dimeric molecule in thallium(I) diisobutyldithiocarbamate. The sulfur plane coincides with the paper plane. The atomic notation is shown.

atom to the four sulfur atoms are 2.966(6), 3.043(5), 3.123(6), and 3.184(5) Å. (see Table 4b and Fig. 3). The line connecting the two thallium atoms is nearly perpendicular to the plane of the sulfur atoms (angle plane-line 87.7°). The metal-metal distance in the dimer is 3.678(2) Å.

The central part (S_1, S_2, C_0, N, C_{11}, C_{21}) of the dithiocarbamate ligand is almost planar; none of the atoms deviates more than 0.05 Å from the calculated least-squares plane (see Table 5). This plane is inclined by 6.6° (dihedral angle) to the central sulfur plane of the dimer. It passes close (0.23 Å) to the centre of the dimer. As is seen from Table 5 the outer parts of the isobutyl groups are situated on opposite sides of the central ligand plane. The nitrogen atom and the atoms C_{11}, C_{12}, C_{13} and C_{21}, C_{22}, C_{23}, respectively, form almost planar zig-zag chains (see also Fig. 1). The dihedral angles between these planes and the central ligand plane are almost equal, 83.3 and 82.5°, respectively.

Coordination. The metal atoms have five-fold sulfur coordination. The coordination poly-
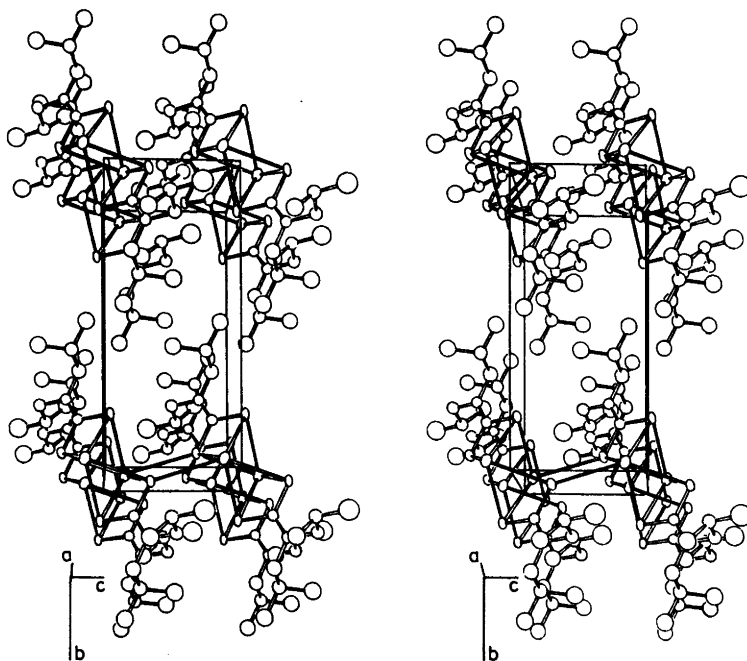

Fig. 2. Stereoscopic illustration of the unit cell. Eight dimers are shown. The linkage is indicated by solid lines between one pair of dimers.
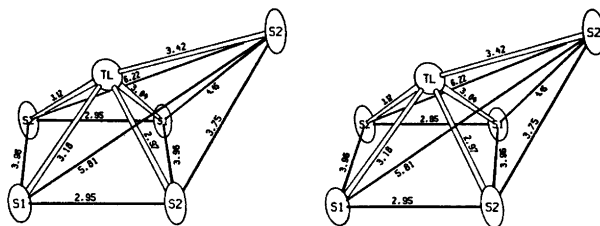
Fig. 3. Stereoscopic illustration of the coordination polyhedron.

hedron is a skew tetragonal pyramid as shown in Fig. 3. The four sulfur atoms in the dimer form the basal plane. The more distant fifth atom belongs to another dimer which is related by a unit translation in the *c* direction. All other sulfur atoms are more than 5.7 Å away. The coordination is such that more than half of the coordination sphere of the thallium atom is empty.

The irregular coordination environments known for a number of thallium(I) compounds have been associated with the outer pair of *s*-electrons $(6s^2)$.[15] Mixed *s-p* metal orbitals may give stabilisation energy in antisymmetric environments. One example is salicylato-(1,10-phenanthroline)thallium(I) [16] where the metal coordination in the dimeric molecules is five-fold, and the coordinated atoms are all situated in one half sphere around the metal atom. The large region free from coordination was attributed to the presence of a stereochemically active $6s^2$ electron pair. This compound is similar to thallium(I) diisobutyldithiocarbamate as to the presence of large ligands.

It is interesting to note that the coordination number increases in the dialkyldithiocarbamates of thallium(I) as the length of ligands decreases. The coordination numbers are thus six and

seven, respectively, in the ethyl and methyl compounds. Also the coordinated atoms become more regularly disposed in space. The shorter ligands allow the metal atoms to coordinate sulfur atoms from other dimeric molecules more easily. This group of compounds evidently represents a case where the irregular coordination environment of thallium(I) may not be attributed solely to the inert electron pair. The packing characteristics of the dimeric molecules strongly influence the structure as will be shown below.

The metal atom arrangement and the linking of the dimers. As mentioned above, the distances between the two thallium atoms in the dimeric unit is 3.68 Å, which is somewhat longer than the interatomic distance in metallic thallium (3.41 Å).[17] There are no other metal-metal distances shorter than 5 Å in the present compound. The metal arrangement thus consists of distinct pairs of thallium atoms.

The thallium dialkyl dithiocarbamates investigated by this research group all contain dimers with similar central parts.[1–5] It is then interesting to find that the arrangements of the metal atoms are quite different. Of the compounds studied the pair arrangement observed in thallium diisobutyldithiocarbamate apparent-

Table 5. Deviations from the least squares planes I, II and III defined by the atoms S_1, S_2, C_0, N, C_{11}, C_{21} (I); N, C_{11}, C_{12}, C_{13} (II); N, C_{21}, C_{22}, C_{23} (III).

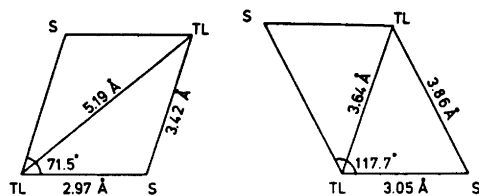| Plane I		Plane II		Plane III	
Atoms	Dev. (Å)	Atoms	Dev. (Å)	Atoms	Dev. (Å)
S_1	0.047	N	0.007	N	0.022
S_2	−0.027	C_{11}	−0.007	C_{21}	0.023
N	−0.004	C_{12}	−0.006	C_{22}	0.019
C_0	−0.026	C_{13}	0.006	C_{23}	−0.020
C_{11}	−0.038				
C_{21}	0.049				

Fig. 4. The linking parallelograms in thallium(I) diisobutyldithiocarbamate (left) and thallium(I) diisopropyldithiocarbamate (right).

ly represents an end point in a breaking-up process starting with the two-dimensional net arrangement found in thallium dimethyldithiocarbamate.[1] The zig-zag chains found in the ethyl,[2] propyl,[3] and the isopropyl[4] compounds are intermediate steps in this process. The metal atom arrangement in these compounds is thus found to change in a consistent way with the length of the alkyl ligands. Apparently the orientation of the dimers with respect to each other is strongly influenced by the ligands.

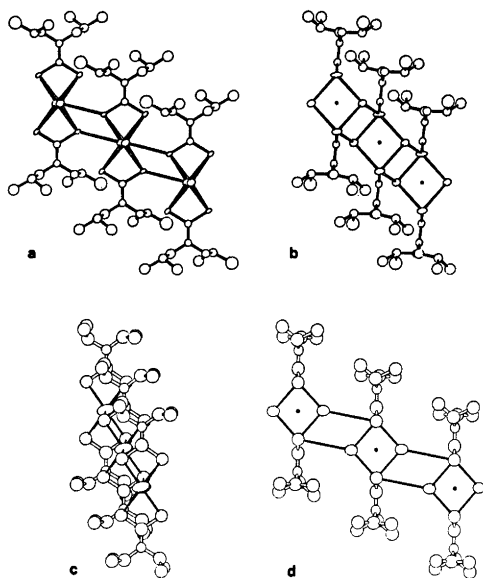An interesting comparison can be made between the isopropyl and the isobutyl com-

pounds. In both cases the dimers are related by translation to form strings along the c-axis. Each thallium atom is coordinated to one sulfur atom in an adjacent dimer at a distance of 3.86 Å in the isopropyl and 3.42 Å in the isobutyl compound. Although the distances between the centres of the dimers are nearly the same, 6.31 Å in the isopropyl and 6.22 Å in the isobutyl compound, the thallium-thallium distances are quite different, 3.64 Å and 5.19 Å, respectively, as shown in Fig. 4. The parallelograms in the figure comprise the two thallium and two sulfur atoms involved in the linkage of each pair of dimers. The edges are similar, but the thallium-thallium distances are considerably different. The difference in orientation of the dimers within the strings is associated with the different space requirements of the ligands as is illustrated by Fig. 5 (a—d). Two mutually perpendicular projections of the isopropyl string are shown in Fig. 5 c and d. The sulfur parallelograms of the dimers are normal to the paper plane in d and the two figures show that the string makes only a small angle (12°) with that plane. The string of isobutyl dimers is shown in Fig. 5 a and b in the same orientation as c and d, respectively. Here the string makes a large angle (49°) with the paper plane of b. This change in direction of the string with respect to the dimers allows the ligands to slide on top of one another. The same molecular separation, the c-axis, as in the isopropyl string is then maintained despite the larger space requirement of the isobutyl ligands. The inclination of the string results in the skew coordination pyramid around the metal atom, Fig. 3, in the isobutyl compound. The coordination pyramid in the isopropyl compound is straight and the bond to the apical sulfur atom is almost normal to the sulfur parallelogram. This clearly demonstrates the connection between molecular packing and metal coordination in this group of compounds.

Fig. 5. The strings of dimers in thallium(I) diisobutyldithiocarbamate (a,b) and thallium(I) diisopropyldithiocarbamate (c,d). The sulfur planes are parallel to the paper in the left figures (a,c) and normal to the paper in the right figures (b,d).

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