Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

The Crystal and Molecular Structure of Tetrakis(thiourea)palladium(II) Chloride

By D. A. BERTA, W. A. SPOFFORD, III, P. BOLDRINI, and E. L. AMMA[1]

Received August 4, 1969

The crystal structure of orthorhombic tetrakis(thiourea)palladium(II) chloride, $Pd[SC(NH_2)_2]_4Cl_2$, has been determined from 1180 counter-measured intensities at room temperature. All atoms, including hydrogen, have been located and refined by full-matrix least squares to a final conventional R of 0.026. Cell constants were found to be: $a = 12.909 \pm 0.003$ Å, $b = 8.256 \pm 0.004$ Å, and $c = 15.175 \pm 0.004$ Å. The space group is $Pna2_1$, with four molecules per cell; $D_c = 1.98$ g cm^{-3} and $D_m = 1.96 \pm 0.02$ cm^{-3}. The structure is composed of molecular $Pd[SC(NH_2)_2]_4{}^{2+}$ ions and Cl^- ions. The thiourea groups are bonded to the metal through sulfur with C–S–Pd angles of approximately 110°, indicating that sulfur uses an sp^2 orbital to form the bond with the metal. The Pd and four S atoms are slightly distorted from the usual square-planar arrangement toward a tetrahedral geometry. Except for this distortion the thiourea groups are arranged about Pd such that the complex ion has an approximate center of symmetry. The average Pd–S distance is 2.334 ± 0.011 Å with individual errors of ±0.003 Å. The shortest Pd–Cl distance is 3.594 ± 0.003 Å. The sulfur–carbon and carbon–nitrogen distances are not significantly different from those of free thiourea. The thiourea groups are tilted away from the approximate plane of the metal and four sulfur atoms ~50° and twisted about the S–C bond ~20°.

Introduction

Thiourea (tu) complexed with transition metal ions gives rise to some interesting and unusual spectroscopic,[2,3] magnetic,[4] and structural properties.[5-9] In $Ag(tu)_2Cl$,[7,8] $Cu(tu)_2Cl$,[9] and $Cu_4(tu)_9(NO_3)_4$[10] delocalized three-center electron pair bonds have been found. (For a more complete introduction see ref 8.) *trans*-$Ni(tu)_4Cl_2$ has been shown to have the molecular symmetry C_4 in which not only are the thiourea molecules arranged about the Ni(II) in an umbrella-like fashion, but also the metal is displaced out of the plane defined by the sulfur atoms toward the chlorine at the handle of the umbrella with an Ni–Cl distance of 2.40 ± 0.02 Å. However, the nickel to chlorine distance at the apex of the umbrella is 2.52 ± 0.02 Å. The geometry defined by the four sulfur and two chlorine atoms may be described as a distortion toward a tetragonal pyramid configuration. This is a rather unusual coordination geometry for Ni(II) and has prompted us to examine the structure of a number of transition metal–thiourea complexes. In addition, there exists a report in the literature[11] that $M(tu)_4Cl_2$ complexes, where M = Ni(II), Fe(II), Co(II), Mn(II), or Cd(II), are all crystallographically isomorphous, and, therefore, all of these complexes have exactly the same geometry as $Ni(tu)_4Cl_2$. We have recently shown[12] that this report is incorrect and $Ni(tu)_4Cl_2$ is structurally unique relative to the other members of the above series. The remaining compounds of the above series are isomorphous and the metal is on a crystallographic center of symmetry with equal metal–chlorine distances. To gain further understanding of the nature of the metal–sulfur interaction in transition metal–thiourea complexes, we decided to examine the structure of $Pd(tu)_4Cl_2$. This particular complex crystallizes in two forms, a monoclinic form, the structure of which has been reported from two-dimensional diffraction data,[13] and the orthorhombic form discussed here. The structure reported for the monoclinic form gives rise to some unusual nonbonded intermolecular distances. We were also interested to see whether these same intermolecular distances were a common feature in the monoclinic and orthorhombic structures.

Experimental Section

Tetrakis(thiourea)palladium(II) chloride, $Pd[SC(NH)_2]_4Cl_2$, was prepared by previously reported methods[14] and single crystals were grown by crystallization from aqueous solution. Two different crystalline modifications were found: (a) a monoclinic form which was frequently twinned for which we never obtained really satisfactory diffraction quality single crystals; (b) an orthorhombic form, for which we were able to obtain good single crystals. Preliminary Weissenberg and precession data showed the orthorhombic crystals to have systematic extinctions: for $0kl$, $k + l = 2n + 1$; for $h0l$, $h = 2n + 1$, indicating the space groups $Pna2_1$, Pnam, or Pmnb.[15] A crystal 0.10 × 0.14 × 0.84 mm was mounted with the needle axis (b) vertical on a Picker automatic diffractometer and aligned by local variations of well-known methods.[16] The cell constants were obtained from a

---

(1) Address all correspondence to this author.

(2) F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).

(3) C. D. Flint and M. Goodgame, *J. Chem. Soc., A*, 1718 (1967).

(4) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964).

(5) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 942 (1956).

(6) A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

(7) E. A. Vizzini and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 2872 (1966).

(8) E. A. Vizzini, I. F. Taylor, Jr., and E. L. Amma, *Inorg. Chem.*, **7**, 1351 (1968).

(9) W. A. Spofford, III, and E. L. Amma, *Chem. Commun.*, 405 (1968).

(10) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 4270 (1966).

(11) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 867 (1956).

(12) J. E. O'Connor and E. L. Amma, *Chem. Commun.*, 892 (1968).

(13) S. Ooi, T. Kawase, K. Nakatsu, and H. Kuroya, *Bull. Chem. Soc. Japan*, **33**, 861 (1960).

(14) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).

(15) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952, pp 119, 151. Pnam = Pmnb with appropriate axial transformations.

(16) (a) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957; (b) K. Knox in "Master Card Program for Picker Four Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland, Ohio, 1967, p 11; (c) W. R. Busing and H. A. Levy, *Acta Cryst.*, **22**, 457 (1967).

TABLE I

RESULTS OF REFINEMENTS[a]

AU	$+z$	$-z$	$R-/R+$
R	0.02566	0.02574	1.003
WR	0.03155	0.03189	1.011
Std error	1.96	1.98	...
AV	$+z$	$-z$	$R-/R+$
R	0.02617	0.02670	1.020
WR	0.02908	0.03006	1.033
Std error	2.12	2.21	...
NA, U	$+z$	$-z$	$R-/R+$
R	0.0257	0.02638	1.015
WR	0.03206	0.03246	1.008
Std error	1.99	2.01	...
NA, V	$+z$	$-z$	$R-/R+$
R	0.02653	0.02673	1.007
WR	0.02976	0.0301	1.013
Std error	2.56	2.63	...

[a] Abbreviations: A, absorption correction applied to data; NA, absorption correction not applied; U, all weights constant at unity; *R*, conventional reliability index;[23] *WR*, weighed *R*;[23] V, variable weighting scheme used. $W = 1/\sigma^2$, $\sigma(F) = (k/2LpF)\cdot[I(\text{scan}) + (1.125)^2(B_1 + B_2) + \{0.04I(\text{scan})\}^2]^{1/2}$, where k is the scale factor, $1/Lp$ is the usual Lorentz and polarization correction, and other quantities are as defined previously. See also S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10,** 70 (1957).

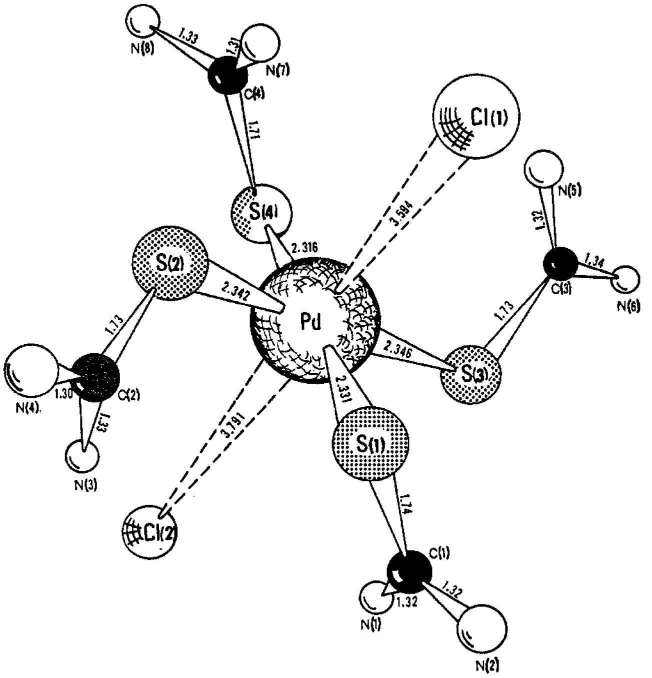

Figure 1.—A perspective view of the $[Pd(tu)_4]^{2+}[2Cl^-]$ structure with the most important distances. The standard deviations (Å) in the above distances are: Pd–S, ±0.003; Pd–Cl, ±0.003; S–C, ±0.011; C–N, ±0.014. For clarity hydrogens are omitted with the N–H distances. See Table III. For the same reason the angles are omitted and are also to be found in Table III.

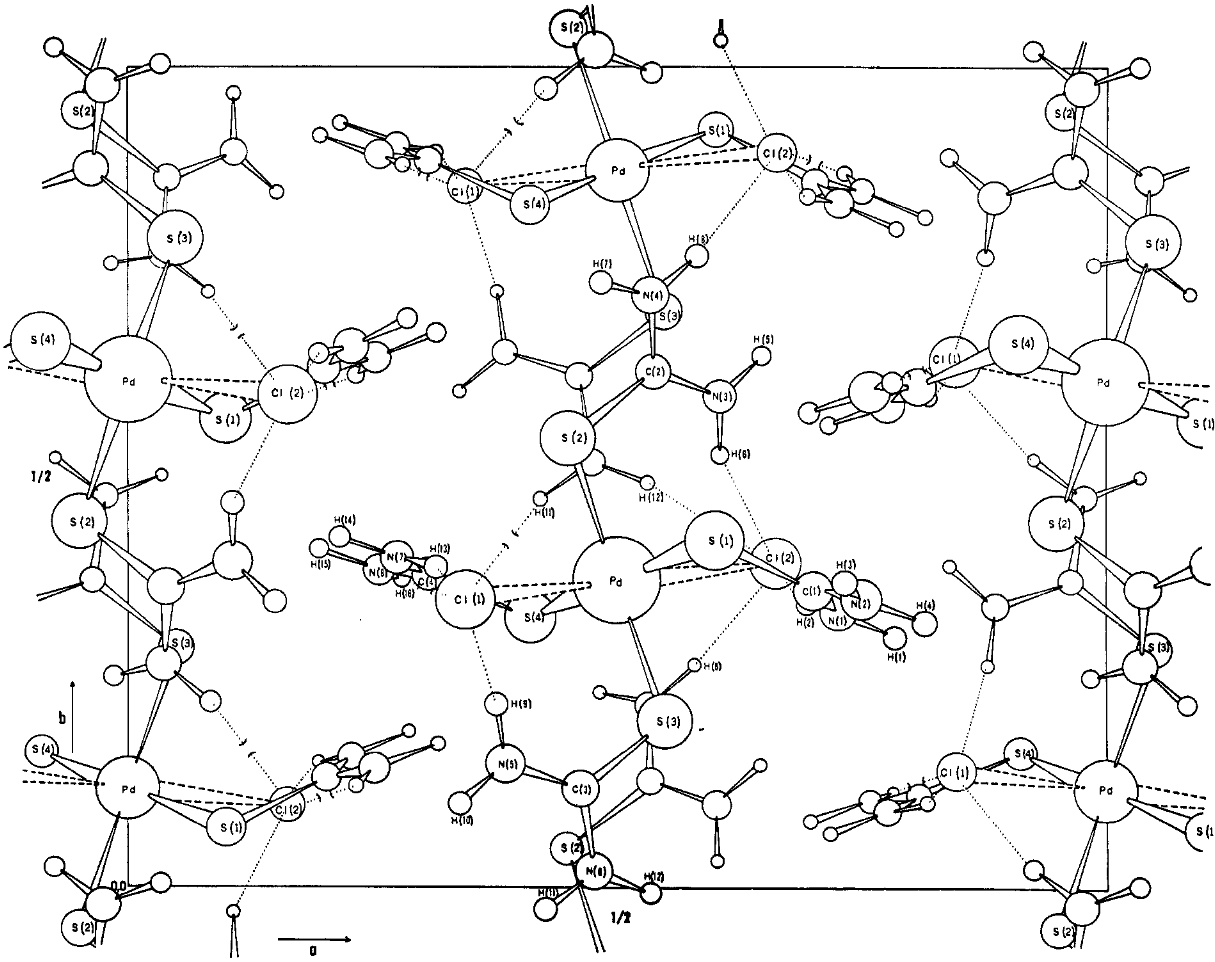

Figure 2.—A perspective view of the unit cell of the $Pd(tu)_4Cl_2$ structure down the *b* axis. The hydrogen-bonding network is shown by dotted lines. For more details on the hydrogen bonding see Table III.

TABLE IIA

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

* 0 0 L *		
4	1382	1401
6	712	723
8	850	814
10	543	552
12	899	905
14	242	211
16	276	267
18	668	667
* 2 0 L *		
1	1743	1663
2	263	261
3	658	730
4	755	740
5	1595	1589
6	1363	1368
7	1156	1186
8	686	657
9	1281	1322
10	343	338
11	1513	1551
12	395	383
13	1371	1377
14	463	467
15	397	367
16	177	183
17	281	264
* 4 0 L *		
1	498	482
3	1934	1945
4	840	823
5	337	326
6	1159	1190
7	651	646
8	1255	1275
10	997	1014
11	252	219
12	1183	1202
13	215	207
14	545	529
16	311	299
17	459	429
* 6 0 L *		
1	2144	2118
2	1213	1209
3	1133	1098
4	327	306
5	1769	1768
6	744	739
7	811	808
10	343	339
11	322	342
12	390	390
13	641	640
14	443	451
15	607	602
17	617	589
* 8 0 L *		
0	1060	1037
2	536	518
3	300	284
4	1260	1261
5	1038	1049
6	1516	1526
7	238	247
8	1018	1024
9	376	383
10	647	678
11	209	209
12	738	736
13	394	413
14	607	594
15	461	415
* 10 0 L *		
1	241	208
2	768	760
3	555	558
4	454	478
5	1183	1175
6	191	177
7	948	958
8	452	440
9	517	510
10	259	252
11	551	550
12	201	197
13	572	548
* 12 0 L *		
0	857	862
2	1015	1034
4	1097	1125
5	397	403
6	838	859
7	342	378
8	222	215
* 14 0 L *		
2	196	187
3	494	506
4	438	448
5	700	693
6	287	281
7	756	762
8	177	171
* 0 1 L *		
1	445	420
3	283	306
5	1267	1334
7	1017	1046
9	611	628
11	392	379
13	355	356
* 1 1 L *		
0	1477	1366
1	1335	1260
2	1373	1174
3	1165	1137
4	1191	1197
5	968	967
6	456	461
7	366	371
8	646	639
9	940	931
10	898	913
11	490	496
12	505	514
13	463	461
14	552	535
15	500	495
16	456	444
17	440	452
18	426	400
* 2 1 L *		
1	200	174
2	524	507
3	175	165
4	1009	1019
5	487	487
7	209	296
8	1174	1199
9	245	243
10	185	178
11	267	283
12	514	526
* 3 1 L *		
0	654	603
1	776	696
2	789	734
3	1039	1034
4	1405	1382
5	1091	1082
6	900	897
7	875	895
8	1007	1017
9	1390	1425
10	1155	1169
11	881	902
12	671	688
13	544	549
14	555	545
15	441	433
16	269	263
17	226	218
* 4 1 L *		
0	243	231
1	259	242
2	820	806
3	491	470
4	607	585
5	835	822
6	801	818
7	554	542
9	338	337
10	662	655
11	242	245
16	200	213
17	195	165
* 5 1 L *		
0	1406	1356
1	1287	1245
2	1459	1426
3	1300	1281
4	1275	1272
5	941	930
6	553	552
7	352	346
8	580	596
9	547	537
10	682	686
11	303	321
12	238	240
13	345	342
14	484	480
15	541	528
16	470	447
17	457	449
* 6 1 L *		
1	193	205
2	234	233
3	388	389
5	671	655
6	241	282
7	448	446
8	251	227
9	345	398
10	181	181
11	400	401
14	250	225
* 7 1 L *		
0	532	532
1	861	840
2	824	808
3	908	985
4	802	896
5	828	825
6	833	840
7	628	647
8	513	516
9	546	541
10	419	404
11	424	436
12	428	449
13	431	432
14	468	461
15	520	530
16	440	432
* 8 1 L *		
0	226	215
1	225	232
2	555	546
3	602	616
4	322	317
6	572	577
9	215	193
10	520	521
13	241	227
* 9 1 L *		
0	242	229
1	333	328
2	478	488
3	525	513
4	698	696
5	730	738
6	782	811
7	714	717
8	827	855
9	716	712
10	827	826
11	652	634
12	539	538
13	426	420
14	472	459
* 10 1 L *		
2	379	361
3	401	402
4	293	291
5	165	183
6	249	254
7	230	228
8	328	322
14	286	270
* 11 1 L *		
0	745	745
1	821	830
2	727	745
3	887	900
4	679	687
5	741	758
6	523	532
7	476	472
8	205	210
9	181	182
10	202	166
11	228	210
12	222	221
13	303	302
* 12 1 L *		
0	460	471
2	193	185
3	322	327
7	267	272
9	210	176
* 13 1 L *		
0	425	448
1	429	438
2	541	548
3	396	396
4	425	430
5	352	362
6	505	510
7	410	418
8	433	405
9	275	265
10	350	358
* 14 1 L *		
1	298	302
3	230	247
4	235	206
8	191	198
* 15 1 L *		
1	200	212
2	196	198
3	289	304
4	249	241
5	487	458
* 0 2 L *		
0	1754	1824
6	1359	1390
8	621	613
10	242	231
12	187	200
14	629	649
16	754	758
* 1 2 L *		
0	416	392
1	900	906
2	879	885
3	544	546
4	530	517
5	566	568
6	205	210
7	248	258
10	236	234
12	161	154
14	293	290
15	186	180
17	217	211
18	203	163
* 2 2 L *		
1	457	458
2	1164	1175
3	1390	1372
4	1027	1025
5	1639	1659
6	688	667
7	1208	1254
8	188	182
9	1383	1412
11	705	721
13	883	878
15	806	795
16	242	237
17	649	647
* 3 2 L *		
0	959	948
1	835	822
2	990	983
3	235	223
4	647	640
5	568	579
6	255	239
7	253	248
9	159	148
10	166	165
12	162	143
14	371	354
16	234	219
* 4 2 L *		
0	246	153
1	439	419
2	1174	1136
4	1383	1383
5	791	784
6	1135	1130
7	902	897
8	1180	1179
9	522	513
10	996	996
12	563	554
13	487	488
14	728	716
15	494	476
16	559	537
* 5 2 L *		
0	401	391
1	371	360
3	496	498
4	372	371
5	424	418
6	191	196
7	305	310
8	292	289
9	239	226
12	309	329
15	208	184
17	203	169
* 6 2 L *		
0	215	215
1	1757	1743
2	772	769
3	1777	1757
4	174	186
5	950	941
7	524	538
8	379	364
9	622	618
10	170	158
11	338	340
12	210	194
13	443	443
14	317	305
15	503	487
* 7 2 L *		
0	421	406
1	561	550
2	364	353
3	196	188
4	414	428
5	263	258
7	286	303
10	219	191
11	206	188
16	192	174
* 8 2 L *		
0	841	840
1	591	585
2	1172	1149
3	755	741
4	718	713
5	359	359
6	732	738
7	224	229
8	1062	1075
10	1147	1142
11	193	172
12	802	792
13	183	172
14	451	455
* 9 2 L *		
0	367	356
3	389	387
4	281	267
6	188	181
7	319	317
8	192	174
9	243	245
12	305	289
* 10 2 L *		
0	264	262
1	751	756
3	608	602
4	460	456
5	271	271
6	381	380
7	593	606
8	204	201
9	889	896
11	899	889
12	174	162
13	620	626
* 11 2 L *		
1	189	184
2	162	173
7	229	208
10	275	267
* 12 2 L *		
0	1319	1323
1	178	204
2	1258	1260
4	573	568
6	323	312
7	166	159
8	318	328
10	351	351
11	194	181
* 13 2 L *		
3	232	260
6	178	185
* 14 2 L *		
1	444	454
3	387	423
5	347	364
6	288	270
7	656	650
* 0 3 L *		
1	595	624
3	820	834
5	488	498
7	540	551
9	237	230
13	481	469
* 1 3 L *		
0	1338	1317
1	1124	1124
2	631	601
3	600	594
4	1221	1220
5	1148	1176
6	1114	1165
7	964	980
8	647	639
9	194	205
10	203	190
11	218	221
12	612	611
13	688	672
14	606	578
15	358	357
16	484	481
17	473	482
* 2 3 L *		
0	735	700
1	395	392
2	226	217
4	338	328
5	243	228
6	472	481
7	234	230
8	460	460
12	254	238
14	203	172
* 3 3 L *		
0	1210	1165
1	702	644
2	193	206
3	437	400
4	829	808
5	1174	1186
6	1101	1127
7	1293	1319
8	1184	1205
9	593	604
10	468	474
11	638	640
12	792	798
13	823	830
14	445	432
15	309	288
16	217	198
17	293	280
* 4 3 L *		
0	364	342
1	479	455
3	440	440
4	260	281
5	400	408
6	281	268
7	383	389
8	215	221
10	295	265
12	219	220
13	287	305
16	220	209
* 5 3 L *		
0	1292	1287
1	1270	1238
2	830	809
3	587	563
4	996	993
5	584	589
6	954	968
7	928	921
8	765	770
9	381	395
10	168	176
11	399	376
12	623	626
13	594	577
14	468	473
15	215	230
16	375	358
* 6 3 L *		
0	320	345
1	497	486
2	201	209
3	185	189
4	224	227
5	443	481
6	241	218
7	340	333
8	237	241
9	248	262
11	256	232
12	217	210
15	194	180
* 7 3 L *		
1	968	944
2	689	676
3	589	587
4	811	828
5	869	876
6	495	500
7	571	577
8	671	669
9	361	373
10	366	376
11	481	496
12	468	468
13	509	513
14	240	249
15	275	277
* 8 3 L *		
0	282	284
1	252	244
2	174	166
3	186	175
4	199	188
7	274	280
8	272	273
9	234	217
13	221	217
* 9 3 L *		
0	460	459
1	498	484
2	518	515
3	344	338
4	375	387
5	326	336
6	560	549
7	818	837
8	839	828
9	703	689
10	710	710
11	628	622
12	724	714
13	454	462
14	301	304
* 10 3 L *		
0	253	247
2	375	372
4	247	261
5	196	217
7	214	203
8	186	181
12	227	217
* 11 3 L *		
0	787	774
1	1021	1008
2	807	811
3	789	789
4	356	362
5	306	323
6	284	282
7	326	344
8	352	353
9	370	378
10	261	281
11	379	381
* 12 3 L *		
1	206	213
3	276	270
7	186	196
* 13 3 L *		
0	432	439
1	317	322
2	515	538
3	401	411
4	386	386
5	389	411
6	359	361
7	342	336
8	396	396
* 14 3 L *		
2	220	195
* 0 4 L *		
0	1917	1970
2	1922	2067
4	1684	1741
6	372	360
8	490	484
10	608	599
12	406	422
14	491	511
* 1 4 L *		
1	607	615
2	801	824
3	603	610
4	337	347
5	484	471
6	196	217
8	257	265
9	418	451
10	331	342
12	216	210
13	185	207
14	224	204
* 2 4 L *		
0	310	319
1	906	909
2	415	420
3	995	1015
4	405	411
5	591	591
6	545	539
7	755	770
8	457	457
9	1362	1387
11	1025	1043
12	198	180
13	690	671
14	232	228
15	498	500
16	237	236
* 3 4 L *		
0	584	572
1	300	297
2	670	679
3	573	581
5	428	423
6	286	269
7	370	352
8	333	324
9	205	191
10	394	391
12	366	360
15	215	237
* 4 4 L *		
0	573	562
1	239	242
2	930	910
3	876	875
4	1068	1078
5	661	668
6	623	622
8	925	930
10	929	940
12	703	715
13	197	188
14	587	570
15	207	211
16	402	404
* 5 4 L *		
0	691	689
1	550	566
2	327	334
3	234	238
4	584	626
5	269	273
6	243	254
8	167	183
9	318	311
11	225	204
13	231	222
14	230	215
* 6 4 L *		
0	492	493
1	1438	1437
2	183	166
3	1302	1306
4	288	289
5	766	763
6	169	176
7	530	514
8	252	236
9	469	465
11	320	323
12	276	273
13	304	296
15	483	466
* 7 4 L *		
0	612	614
1	186	166
3	519	522
4	169	159
5	380	378
7	403	393
8	292	301
12	293	287
* 8 4 L *		
0	387	394
1	242	241
2	645	638
3	216	206
4	870	867
5	237	241
6	865	883
7	538	534
8	876	879
9	343	338
10	699	699
11	177	178
12	552	572
13	220	200
14	473	449
* 9 4 L *		
0	418	418
1	261	281
3	208	205
4	405	385
5	194	215
6	182	178
7	317	295
8	208	227
13	288	295
* 10 4 L *		
1	347	355
3	575	578
4	482	467
5	627	662
6	343	332
7	732	741
9	535	522
11	479	483
* 11 4 L *		
0	199	201
2	265	258
3	334	318
4	194	192
6	261	259
8	227	224
* 12 4 L *		
0	769	767
2	811	806
4	707	709
6	604	611
8	304	302
* 13 4 L *		
3	213	217
5	274	269
7	238	248
* 14 4 L *		
1	225	222
2	231	233
* 0 5 L *		
1	591	643
3	326	345
5	339	330
9	500	493
11	472	466
13	214	204
15	184	204
* 1 5 L *		
0	970	1015
1	948	996
2	836	859
3	789	814
4	434	450
5	432	438
6	334	351
7	196	200
8	371	389
9	602	605
10	712	727
11	516	530
12	379	373
13	322	331
14	406	388
15	271	271
* 2 5 L *		
0	569	573
2	636	644
3	182	242
8	343	328
10	587	593
12	178	184
14	320	303
* 3 5 L *		
0	456	440
1	714	735
2	592	571
3	521	536
4	689	690
5	463	461
6	419	404
7	599	609
8	717	704
9	841	848
10	911	911
11	758	770
12	511	512
13	389	391
14	363	354
15	193	191
* 4 5 L *		
0	236	240
1	471	471
2	209	198
3	372	388
4	319	322
5	432	440
6	193	180
8	311	317
9	375	376
11	331	336
12	176	164
13	212	192
15	210	217
* 5 5 L *		
0	903	868
1	564	541
2	886	885
3	907	902
4	593	607
5	714	718
6	574	585
7	189	168
8	338	325
9	427	438
10	421	405
11	281	272
12	224	248
13	296	310
14	246	241
* 6 5 L *		
0	198	179
1	225	225
2	359	337
3	302	314
4	254	255
5	180	157
6	227	220
7	268	271
8	284	281
9	191	200
10	300	281
14	206	214
* 7 5 L *		
0	277	249
1	571	566
2	534	533
3	417	432
4	656	663
5	551	565
6	479	481
7	589	582
8	537	534
9	325	327
10	347	346
11	304	317
12	331	346
13	356	355
* 8 5 L *		
0	185	200
3	267	261
4	371	372
5	482	473
7	247	244
8	164	170
9	170	161
12	187	198
* 9 5 L *		
2	201	203
3	538	542
4	506	515
5	652	645
6	796	797
7	406	399
8	458	457
9	467	476
10	360	366
11	317	325
12	375	366
* 10 5 L *		
1	213	238
2	178	178
3	211	205
4	340	350
6	344	351
8	172	185
* 11 5 L *		
0	299	278
1	574	553
2	501	488
3	477	479
4	546	548
5	634	634
6	311	326
7	453	449
8	216	227
* 12 5 L *		
3	186	172
5	313	317
7	224	213
* 13 5 L *		
0	241	254
1	192	216
2	337	343
3	465	451
4	406	409
* 0 6 L *		
0	1684	1682
2	945	955
4	739	777
6	852	864
8	563	585
12	374	376
14	317	303
* 1 6 L *		
0	654	652
1	477	455
2	273	272
3	274	284
5	548	548
6	265	275
7	347	347
8	294	298
9	204	197
10	200	196
12	382	360
13	221	233
* 2 6 L *		
1	773	763
3	242	253
4	410	399
5	822	833
6	420	401
7	887	896
9	668	678
10	192	177
11	554	551
13	545	530
* 3 6 L *		
0	354	375
1	534	528
4	176	186
5	194	194
6	454	454
8	277	288
9	189	187
11	251	241
12	238	240
13	178	189
* 4 6 L *		
0	794	783
1	287	295
2	364	350
3	375	362
4	523	532
5	250	244
6	875	873
7	325	301
8	679	672
10	506	505
11	226	202
12	600	600
* 5 6 L *		
0	602	636
2	233	224
5	625	618
7	342	350
10	267	263
12	280	293
13	178	186
* 6 6 L *		
0	249	262
1	1097	1078
2	214	203
3	680	661
4	222	254
5	769	773
6	234	262
7	490	494
8	206	191
10	182	192
11	179	188
* 7 6 L *		
0	255	261
1	419	414
2	242	247
4	267	273
5	212	194
6	417	427
7	232	234
9	176	167
11	301	299
* 8 6 L *		
0	471	481
2	405	384
3	196	174
4	565	548
5	496	479
6	705	702
8	542	546
10	510	520
* 9 6 L *		
0	254	258
1	212	209
3	208	221
4	191	189
5	361	362
7	207	217
8	234	229
* 10 6 L *		
1	435	438
2	197	203
3	431	423
5	493	508
7	434	440
8	304	306
* 11 6 L *		
2	230	259
6	204	206
* 12 6 L *		
0	660	651
2	627	607
* 0 7 L *		
3	498	500
5	475	487
7	372	390
9	280	274
* 1 7 L *		
0	234	237
1	331	335
2	489	482
3	591	590
4	521	548
5	713	733
6	344	337
7	368	379
8	441	467
9	215	229
10	232	254
* 2 7 L *		
2	251	270
4	696	698
6	287	293
8	286	319
10	170	153
* 3 7 L *		
0	209	232
3	606	595
4	538	532
5	509	505
6	487	498
7	465	456
8	646	647
9	457	454
10	334	325
11	342	355
12	271	258
* 4 7 L *		
1	200	176
2	382	367
3	470	478
5	345	345
6	176	177
7	315	319
9	325	326
* 5 7 L *		
0	376	362
1	442	443
2	702	696
3	360	351
4	431	427
5	512	493
6	282	272
7	374	301
8	263	269
9	255	252
10	323	322
* 6 7 L *		
0	238	247
1	294	270
2	287	273
3	216	213
4	333	322
6	237	219
8	266	271
10	259	263
* 7 7 L *		
0	577	593
1	414	412
2	287	288
3	616	592
4	386	383
5	176	175
6	317	318
8	281	293
9	316	320
* 8 7 L *		
0	306	293
1	345	342
2	260	250
3	277	286
* 9 7 L *		
1	349	351
2	404	420
4	231	184
5	300	292
7	350	322
* 10 7 L *		
0	455	460
1	180	154
2	301	298
* 0 8 L *		
0	534	509
2	665	678
4	693	716
6	394	406
8	370	380
10	216	223
* 1 8 L *		
1	182	171
2	218	224
3	433	427
4	263	261
5	196	222
6	261	268
7	252	253
8	278	265
9	185	198
* 2 8 L *		
1	361	374
2	198	182
3	615	629
4	217	192
5	560	561
6	261	226
7	485	482
9	411	401
* 3 8 L *		
2	291	294
3	405	397
4	199	204
5	288	272
7	270	267
* 4 8 L *		
0	242	234
2	429	417
4	466	460
5	294	289
6	378	365
7	315	300
8	447	449
9	256	244
* 5 8 L *		
1	265	254
2	191	193
3	351	339
4	181	169
6	277	259
8	217	209
* 6 8 L *		
1	692	679
3	635	617
5	372	360
6	348	328
7	230	255
* 7 8 L *		
2	355	343
3	242	228
5	228	215
* 8 8 L *		
0	304	287
2	420	402
3	189	193
4	280	256
* 0 9 L *		
1	520	517
7	334	343
* 1 9 L *		
0	358	345
1	464	468
2	316	313
3	201	212
4	254	248
5	200	196
6	204	234
7	266	253
* 2 9 L *		
0	572	556
2	273	283
6	321	325
* 3 9 L *		
0	369	381
1	213	178
2	310	276
3	185	196
5	294	288
6	191	198
* 4 9 L *		
1	431	431
2	245	222
* 5 9 L *		
0	228	255
1	458	451
2	323	299
4	356	314
* 6 9 L *		
0	261	263
1	324	263
2	213	199
* 0 10 L *		
0	418	409
2	363	364
4	304	309
8	335	315
10	238	241
* 1 10 L *		
1	257	258
2	212	199
3	254	250
9	244	239
10	241	246
* 2 10 L *		
1	291	312
3	277	280
5	255	273
7	377	354
9	319	302
* 3 10 L *		
1	236	188
3	272	244
9	218	230
* 4 10 L *		
0	220	197
2	254	230
4	237	235
6	220	238
8	331	321
* 5 10 L *		
3	209	205
4	241	233
9	211	197
* 6 10 L *		
1	384	370
3	345	342
5	310	295
7	243	216
* 7 10 L *		
3	197	199
4	263	265

[a] First column is l, followed by F_o and F_c. $F_o/10$ is absolute.

least-squares refinement of the χ, ϕ, and 2θ angles[17] of 25 general reflections with Mo Kα radiation (λ 0.71068 Å) at room temperature; the values obtained are $a = 12.909 \pm 0.003$ Å, $b = 8.256 \pm 0.004$ Å, and $c = 15.175 \pm 0.004$ Å. With four $Pd(tu)_4Cl_2$ units per cell the calculated density is 1.98 g cm^{-3}, in good agreement with the observed value of 1.96 ± 0.02 g cm^{-3} measured by flotation in a carbon tetrachloride–bromoform mixture. With Zr-filtered Mo Kα radiation 1626 independent ***hkl*** intensity data were measured from the above crystal. Backgrounds were measured at $2\theta \pm 0.75°$ from the peak maximum for 40 sec and the peaks were scanned for 90 sec (1.5° 2θ) by the usual θ–2θ scan. The source to crystal distance was 18 cm while the crystal to counter distance was 26 cm. The takeoff angle was 3.7° and the counter aperture was 6 mm × 8 mm high. The incident beam and receiving collimators were both 1.5 mm in diameter. A random sampling of 50 reflections gave no significant systematic variation in symmetry-related reflections of the orthorhombic system (±3%). In particular, we examined ***hkl*** and $hk\bar{l}$ reflections, for if the correct space group were the polar $Pna2_1$ and anomalous dispersions were important, the chirality of the crystal could be determined by such differences. No statistically significant differences were found between 50 ***hkl*** and $hk\bar{l}$ pairs. Therefore, we measured only the crystallographically independent ***hkl*** octant. Although on a purely statistical basis the refinement of the structure leads to a determination of the correct enantiomer (*vide infra*), the difference is sufficiently small that extreme care would have been needed to detect the difference in measured intensities of ***hkl*** and $hk\bar{l}$ reflections. The width at half-peak height of an average reflection is $\sim 0.2°$ 2θ. This value only indicates that the peak was completely covered in the scan range and is not necessarily the mosaic spread. The counting rate never exceeded 5000 counts/sec. Reflections were examined to a 2θ maximum value of 60°. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - 1.125(B_1 + B_2)$, where $I(\text{scan})$ is the number of counts over the scan range and B_1 and B_2 are the background counts. A standard reflection was measured after every tenth reflection to monitor the stability of operation and any crystal decomposition that might occur. With $\sigma[I(\text{net})] = [I(\text{scan}) + (1.125)^2(B_1 + B_2)]^{1/2}$ the variation in $I(\text{net})$ of the standard reflection was less than σ during the period of data collection. However, the variation between measurements of the standard reflection was much less than this and most frequently 0.1σ. A reflection was considered above background when $I(\text{net})$ was greater than $2[(1.125)^2(B_1 + B_2)]^{1/2}$. By this criterion 1180 nonzero ***hkl*** reflections were retained. The linear

---

[17] The least-squares fit to compute the lattice dimensions is a program based upon ref 16 by W. A. Spofford, III, for the IBM 1620. ω_0, χ_0, $2\theta_0$ are fixed machine constants.

absorption coefficient (μ) for Mo Kα radiation was calculated to be 19.4 cm^{-1}. The crystal was approximated by a regular parallelepiped and transmission factors were calculated[18] and found to vary from 0.851 to 0.832. Lorentz and polarization corrections were made and the intensities were reduced to structure factors.

Structure Determination

The space group was established as Pna2$_1$ and the structure was solved by the location of the crystallographically independent Pd, four S, and two Cl atoms from an unsharpened three-dimensional Patterson[19] function. The carbon and nitrogen atoms were located from the three-dimensional electron density function with phases based upon the Pd, S, and Cl atomic positions. The structure was refined by full-matrix[20] least squares with scattering factors from a standard source[21] including real and imaginary dispersion corrections for the Pd, S, and Cl atoms.[22] The isotropic refinement converged to an R value of 0.08. Refinement with only the Pd atom anisotropic yielded an R of 0.065. Several cycles of refinement with all temperature factors anisotropic converged to a final R of 0.029, weighted R of 0.033, and standard error of 2.11.[23] This portion of the structure determination was carried out using unit weights but not absorption corrections.

A three-dimensional difference map clearly resolved all the hydrogen atoms of the thiourea groups. Our earlier experiences,[12,24] which demonstrated that hydrogen atoms could be located and refined by least squares, led us to do likewise in this case. With the inclusion of hydrogen atom coordinates[25] and isotropic temperature factors, eight different refinements were carried out and the results are summarized in Table I. These results, coupled with the fact that the parameters of all of the $+z$ refinements are not significantly different from one another, nor are the $-z$ refinement parameters different from one another (less than one standard deviation), mean the conclusions are independent of absorption corrections and weighting scheme. However, using Hamilton's[26] R factor test the $-z$ refinement can be rejected at least at the 97.5% confidence level depending upon which refinement is used and whether R or weighted R is used in the test. Considering the relatively small changes in R between $+z$ and $-z$ it is not surprising that no systematic differences in intensity were noticed between hkl and $hk\bar{l}$ reflections. The hydrogen parameters refined smoothly with a damping factor of 0.3. Considering the additional number of parameters involved with the inclusion of hydrogen atoms the relatively small decrease in R is disappointing. It is interesting to note that in this case in contrast to others[27,28] the bond lengths derived from the $+z$ and $-z$ refinements do not differ by more than two standard deviations. The scale factor was also treated as a variable along with the atomic parameters. The refinement was terminated when the maximum parameter shifts were less than $^1/_{10}\sigma$ for the nonhydrogen parameters and $^1/_3\sigma$ for the hydrogen parameters. The largest peaks in a final difference map were less than one-fourth the height of the hydrogen peaks in the earlier difference Fourier functions.

The listing of observed and calculated as well as unobserved structure factors is found in Table II. Final atomic coordinate and thermal parameters are enumerated in Table III. Interatomic distances, angles, and errors[29] are listed in Table IV. Table V contains the rms displacements and appropriate least-squares

TABLE IIB

UNOBSERVED REFLECTIONS WITH CALCULATED VALUES GREATER THAN F_{min}[a]

$F_{\text{MIN}} \leq |F(\text{CALC})| < 2.0 \times F_{\text{MIN}}$ (135)

K = 0	14 11 170	10 14 165	10 14 208	13 5 326	12 6 322	8 7 240
8 17 168	15 0 194	11 12 298	11 12 210	13 7 266	12 8 243	8 9 169
10 16 233	15 12 325	11 13 216	11 14 190	13 8 226	12 10 248	K = 9
12 15 210	15 14 211	11 14 179	12 11 171	13 9 234	12 12 230	4 5 179
14 1 197	15 15 248	11 16 176	12 12 173	13 12 247	K = 7	5 3 174
14 17 264	K = 2	12 9 211	12 14 266	13 14 310	7 7 230	5 6 290
K = 1	1 9 209	12 11 177	13 1 177	K = 6	7 10 180	6 4 167
4 14 174	8 16 230	12 13 170	13 10 250	0 10 174	8 9 326	6 6 326
6 17 176	8 17 266	13 9 258	13 13 185	4 9 176	8 11 264	K = 10
8 17 222	10 16 190	13 11 286	14 4 196	5 1 176	9 6 183	0 6 176
9 16 326	10 17 285	13 13 301	14 10 181	5 8 193	10 8 226	1 0 185
9 17 200	12 14 264	13 14 270	14 15 294	6 9 166	10 10 260	1 8 202
10 1 165	12 16 271	13 15 277	K = 5	8 11 217	K = 8	3 2 184
11 14 271	13 1 184	13 16 230	2 4 169	9 10 176	3 8 191	3 4 182
11 16 300	14 12 214	K = 4	8 2 165	9 12 169	5 9 292	3 8 183
11 17 302	14 15 281	5 7 171	9 13 322	10 12 178	6 9 230	5 2 166
12 13 194	K = 3	7 15 267	11 10 165	11 1 166	7 0 188	5 7 180
13 11 323	7 16 300	8 15 215	11 11 166	11 5 194	7 4 169	5 8 206
13 13 233	8 16 173	9 14 178	11 13 185	11 7 242	7 7 221	7 6 204
13 15 267	9 16 165	10 2 188	11 14 239	11 10 201	7 8 171	7 8 174
13 17 245	10 9 165	10 12 194	12 4 174	12 5 182	8 6 308	

$2.0 \times F_{\text{MIN}} \leq |F(\text{CALC})| < 3.0 \times F_{\text{MIN}}$ (41)

K = 0	11 15 405	15 11 427	2 10 369	14 11 440	10 11 423	K = 8
10 17 488	13 12 350	15 13 342	13 10 449	14 13 371	10 13 395	8 8 461
12 14 350	13 14 350	K = 2	13 12 407	K = 5	12 4 471	
14 13 338	13 16 359	10 14 423	K = 4	7 14 369	K = 7	
14 15 465	15 6 407	10 15 340	10 13 441	9 14 374	7 11 350	
K = 1	15 8 384	12 12 371	10 15 443	K = 6	9 8 349	
7 17 426	15 9 411	14 8 365	14 3 408	6 13 340	9 9 362	
9 15 362	15 10 393	K = 3	14 9 444	10 9 393	9 11 342	

$3.0 \times F_{\text{MIN}} \leq |F(\text{CALC})|$ (20)

K = 0	10 15 748	K = 1	0 42850	14 13 514	14 5 573	K = 6
0 21929	12 16 579	15 7 507	6 17 616	K = 3	14 7 655	8 12 529
4 03605	14 9 700	K = 2	14 9 684	7 01085	K = 5	K = 7
8 16 522	14 11 616	0 22882	14 11 699	K = 4	13 6 517	9 10 500

[a] First column is h, followed by l and F_c on the same scale as Table IIA. The number of reflections less than F_{min} is 250. Reflections for which the backgrounds could not be reliably estimated due to β radiation or to white radiation were omitted from the calculations and are included here with the unobserved reflections. The same procedure was used for reflections which were obviously in error due to electronic or equipment malfunction. Unobserved reflections were not included in the refinement.

---

(18) Program for absorption corrections is a local modification by W. A. Spofford, III, of GONO9 written by W. C. Hamilton.

(19) Patterson and electron density calculations done on an IBM 7040 with ERFR-3 program, a modification of the Sly–Schoemaker–Van den Hende ERFR-2 program by D. R. Harris.

(20) Least-squares refinement performed with the ORFLS program of W. Busing, K. O. Martin, and H. Levy (Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962) with local modifications.

(21) (a) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965); (b) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(22) Anomalous dispersion corrections made to F_c, as suggested by J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(23) $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$, weighted $R = [\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma wF_o^2]^{1/2}$, and standard error $= |\Sigma w(F_o - F_c)^2/(N_o - N_v)|^{1/2}$, where $N_o = 1180$ and $N_v = 173$. Unobserved reflections were not used in the refinement. F_o and F_c are on an absolute scale and the weights are normalized to this scale.

(24) M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, **8**, 424 (1969).

(25) H atom scattering factors from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(26) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(27) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

(28) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966).

(29) Distances, angles, and errors computed with the ORFFE program of W. Busing, K. O. Martin, and H. Levy with local modifications on the IBM 7040.

TABLE III

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS[a]

Atom	x	y	z
Pd	0.12359 (5)	−0.01084 (8)	0.0000 (–)
S(1)	0.0746 (2)	0.1889 (03)	0.1002 (2)
S(2)	−0.0477 (2)	−0.0045 (04)	−0.0506 (2)
S(3)	0.2953 (2)	0.0048 (04)	0.0499 (2)
S(4)	0.1677 (2)	−0.2273 (03)	−0.0895 (2)
Cl(1)	0.1467 (2)	0.3140 (03)	−0.1565 (3)
Cl(2)	0.1010 (3)	−0.3577 (03)	0.1626 (2)
C(1)	0.1338 (8)	0.1534 (12)	0.2015 (7)
N(1)	0.1612 (7)	0.0067 (11)	0.2281 (6)
N(2)	0.1458 (8)	0.2796 (10)	0.2535 (7)
C(2)	−0.1309 (9)	−0.0480 (12)	0.0355 (7)
N(3)	−0.1024 (8)	−0.1381 (12)	0.1040 (7)
N(4)	−0.2238 (8)	0.0160 (14)	0.0336 (8)
C(3)	0.3785 (9)	0.0429 (11)	−0.0367 (7)
N(5)	0.3481 (7)	0.0991 (11)	−0.1141 (6)
N(6)	0.4786 (7)	0.0117 (12)	−0.0224 (6)
C(4)	0.1166 (9)	−0.2024 (12)	−0.1929 (7)
N(7)	0.0956 (8)	−0.0583 (11)	−0.2251 (6)
N(8)	0.1055 (8)	−0.3324 (10)	−0.2437 (7)
H(1)	0.190 (11)	−0.007 (18)	0.283 (10)
H(2)	0.151 (11)	−0.073 (17)	0.190 (10)
H(3)	0.126 (11)	0.370 (16)	0.241 (10)
H(4)	0.169 (10)	0.274 (13)	0.318 (09)
H(5)	−0.143 (13)	−0.179 (19)	0.142 (11)
H(6)	−0.032 (12)	−0.186 (16)	0.101 (09)
H(7)	−0.232 (10)	0.115 (17)	−0.014 (10)
H(8)	−0.264 (10)	−0.014 (17)	0.076 (09)
H(9)	0.281 (11)	0.143 (16)	−0.120 (09)
H(10)	0.396 (10)	0.119 (14)	−0.162 (08)
H(11)	0.525 (09)	0.057 (14)	−0.078 (09)
H(12)	0.506 (10)	−0.050 (16)	0.034 (09)
H(13)	0.109 (09)	0.031 (14)	−0.189 (09)
H(14)	0.082 (09)	−0.049 (13)	−0.284 (08)
H(15)	0.089 (15)	−0.314 (18)	−0.301 (13)
H(16)	0.118 (10)	−0.434 (15)	−0.226 (08)

Anisotropic Temperature Factors in the Form

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	B, Å^2
Pd	18.5 (3)	78.0 (9)	17.4 (2)	4.0(6)	0.1 (3)	−4.8 (7)	H(1)	4 (07)
S(1)	33 (2)	85 (04)	22 (1)	16 (2)	−3 (1)	−4 (2)	H(2)	3 (08)
S(2)	23 (2)	203 (06)	25 (1)	10 (3)	−1 (1)	−8 (3)	H(3)	3 (08)
S(3)	21 (2)	142 (05)	19 (1)	3 (2)	−1 (1)	−2 (2)	H(4)	2 (06)
S(4)	32 (2)	81 (04)	19 (1)	9 (2)	−3 (1)	−4 (2)	H(5)	8 (10)
Cl(1)	47 (2)	89 (04)	49 (2)	11 (2)	8 (2)	5 (2)	H(6)	5 (07)
Cl(2)	63 (2)	99 (04)	36 (1)	7 (3)	−3 (2)	−3 (2)	H(7)	5 (07)
C(1)	18 (7)	106 (15)	19 (5)	−3 (8)	0 (4)	2 (7)	H(8)	4 (07)
N(1)	35 (5)	83 (12)	33 (4)	7 (8)	−2 (4)	−5 (7)	H(9)	4 (07)
N(2)	46 (7)	94 (14)	32 (5)	12 (8)	−14 (5)	−14 (7)	H(10)	3 (06)
C(2)	30 (6)	107 (15)	32 (5)	−16 (9)	−4 (6)	−19 (7)	H(11)	3 (06)
N(3)	50 (8)	128 (15)	39 (5)	−19 (8)	2 (5)	−7 (8)	H(12)	3 (06)
N(4)	28 (6)	217 (21)	56 (7)	2 (9)	15 (5)	−23 (9)	H(13)	2 (06)
C(3)	24 (6)	86 (14)	33 (4)	−4 (9)	8 (6)	−17 (7)	H(14)	2 (05)
N(5)	34 (6)	135 (15)	27 (4)	3 (8)	0 (4)	9 (7)	H(15)	5 (10)
N(6)	21 (5)	159 (15)	31 (6)	−6 (8)	0 (4)	17 (8)	H(16)	3 (06)
C(4)	30 (7)	97 (15)	21 (5)	1 (9)	6 (5)	−2 (7)		
N(7)	50 (7)	115 (14)	20 (4)	20 (9)	−12 (4)	1 (7)		
N(8)	41 (7)	101 (14)	27 (5)	19 (8)	−5 (5)	−17 (7)		

[a] The esd of the last figure is in parentheses.

planes.[30] Although the over-all general agreement is good with the relatively small agreement index of less than 0.03, the long needle crystal which may not have been effectively scattering over the entire length introduces some systematic errors and makes our estimates of error somewhat optimistic. This systematic error can be seen in the magnitude of β_{22}, which is considerably larger than either β_{11} or β_{33}.

Description and Discussion of Structure

The crystal structure of $Pd(tu)_4Cl_2$ is made up of complex ions, $Pd(tu)_4^{2+}$, with two essentially ionic

---

(30) Least-squares planes calculated on the IBM 1620 with a program by W. A. Spofford, III.

axial chlorine atoms at distances of 3.594 (3) Å (number in parentheses here and later denotes error in least significant digit) and 3.791 (3) Å. See Figures 1 and 2 and Table IV. The complex ions and the halide ions are interconnected by $N\text{-}H\cdots Cl$ hydrogen bonding to form a sheet structure (Figure 2). These sheets are then held together by ordinary van der Waals forces. The Pd and four S atoms are almost coplanar with a small tetrahedral distortion of approximately 0.1 Å. The arrangement of ligands about Pd is such that the Pd defines an approximate molecular center of symmetry that is not demanded by space group requirements. The Pd–S distances vary between 2.316 and 2.346 Å, all ±0.003 Å or less. Our estimates of error are probably somewhat optimistic due to neglect of systematic errors. These differences do not appear to be significant, but they are somewhat shorter than the 2.36 Å expected from the sum of the single-bond covalent radii.[31] In spite of the fact that the S–Pd bond is a donor–acceptor bond, the bond length is essentially that of a normal single bond or perhaps very slightly shorter. On the other hand, the Pd–Cl distances are at least 1 Å longer than a normal single-bond distance, and the interaction must be viewed as ionic. The S–C distances, averaging 1.73 (1) Å, are probably not significantly different from one another nor from the 1.720 (9) Å S–C distance found by Truter for free thiourea.[32] The neutron diffraction results of Elcombe and Taylor[33] for free thiourea yield an S–C distance of 1.746 (9) Å. Our C–N distances are also not significantly different from Truter's value of 1.340 (6) Å. The neutron diffraction value for the C–N distance is 1.350 (4) Å. The S–C–N angles on the side toward the metal always seem to be greater than those S–C–N distances pointed away from the metal. This fact has been noted previously,[12] but we still lack an explanation for this phenomenon. The N–H distances are reasonable and the thiourea groups are all planar.

TABLE IV
Interatomic Distances, Angles, and Esd's
Not in the Figures[a]

Atoms	Angle, deg	Atoms	Angle, deg
S(1)–Pd–S(2)	86.7 (1)	Pd–S(1)–C(1)	109.7 (4)
S(1)–Pd–S(3)	90.4 (1)	Pd–S(2)–C(2)	109.5 (4)
S(1)–Pd–S(4)	174.5 (1)	Pd–S(3)–C(3)	110.6 (4)
S(1)–Pd–Cl(1)	85.8 (1)	Pd–S(4)–C(4)	110.5 (4)
S(1)–Pd–Cl(2)	95.1 (1)	S(1)–C(1)–N(1)	122.7 (8)
S(2)–Pd–S(3)	175.6 (1)	S(1)–C(1)–N(2)	116.6 (8)
S(2)–Pd–S(4)	93.3 (1)	N(1)–C(1)–N(2)	120.6 (10)
S(2)–Pd–Cl(1)	81.1 (1)	S(2)–C(2)–N(3)	122.4 (9)
S(2)–Pd–Cl(2)	99.1 (1)	S(2)–C(2)–N(4)	117.9 (9)
S(3)–Pd–S(4)	90.0 (1)	N(3)–C(2)–N(4)	119.7 (11)
S(3)–Pd–Cl(1)	95.4 (1)	S(3)–C(3)–N(5)	123.8 (9)
S(3)–Pd–Cl(2)	84.5 (1)	S(3)–C(3)–N(6)	116.3 (8)
S(4)–Pd–Cl(1)	99.6 (1)	N(5)–C(3)–N(6)	119.9 (10)
S(4)–Pd–Cl(2)	79.5 (1)	S(4)–C(4)–N(7)	121.9 (8)
Cl(1)–Pd–Cl(2)	179.2 (1)	S(4)–C(4)–N(8)	118.4 (8)
		N(7)–C(4)–N(8)	119.5 (11)

Nonbonded distances (intramolecular)	Value, Å
S(1)–S(2)	3.207 (4)
S(1)–S(3)	3.319 (4)
S(2)–S(4)	3.386 (4)
S(3)–S(4)	3.296 (4)

Hydrogen-Bonded Distances, Å[b]

H bond	Cl–N	Cl–H
Cl(1)—H(9)–N(5)	3.213 (9)	2.30 (10)
Cl(1)—H(13)–N(7)	3.312 (10)	2.44 (10)
Cl(1)—H(11)–N(6)[c]	3.304 (10)	2.24 (11)
Cl(1)—H(16)–N(8)[c]	3.249 (9)	2.37 (10)
Cl(2)—H(2)–N(1)	3.263 (10)	2.47 (10)
Cl(2)—H(6)–N(3)	3.311 (11)	2.41 (11)
Cl(2)—H(8)–N(4)[c]	3.265 (11)	2.42 (11)
Cl(2)—H(12)–N(6)[c]	3.463 (10)	2.42 (11)

Dihedral Angles between Various Planes

Angle of tilt	Value, deg
[Pd–S(1)–C(1)]–[Pd–S(1)–S(3)]	42.6 (4)
[Pd–S(2)–C(2)]–[Pd–S(2)–S(1)]	58.2 (4)
[Pd–S(3)–C(3)]–[Pd–S(3)–S(4)]	60.7 (4)
[Pd–S(4)–C(4)]–[Pd–S(4)–S(2)]	42.8 (4)
Angle of twist	**Value, deg**
[Pd–S(1)–C(1)]–[S(1)–C(1)–N(1)]	27.4 (10)
[Pd–S(2)–C(2)]–[S(2)–C(2)–N(3)]	27.1 (9)
[Pd–S(3)–C(3)]–[S(3)–C(3)–N(5)]	17.2 (10)
[Pd–S(4)–C(4)]–[S(4)–C(4)–N(7)]	25.9 (11)

[a] All N–H distances are within less than one standard deviation (±0.13 Å) of the average of 0.99 Å. All C–N–H angles are within less than one standard deviation (±4°) of the average of 120°. All H–N–H angles are within less than one standard deviation (±12°) of the average of 120°. [b] All the Cl–H–N hydrogen-bonded angles are 180° within 2.5 standard deviations (10°). [c] H bonds between adjacent molecules.

The Pd–S–C angles are all 110° within two standard deviations (±0.4°). The planar thiourea groups are displaced from the plane defined by the palladium and four sulfur atoms by what might be described as two distortions: (1) a simple rotation (tilt) of the planar group by 43–64° about the Pd–S bond [see (Pd–S–S)–(Pd–S–C) dihedral angles]; (2) a rotation or twist of the thiourea group about the S–C bond by 17–28° [see (Pd–S–C)–(S–C–N) dihedral angles]. The metal–sulfur–carbon angle found in transition metal–thiourea complexes varies between 106 and 116°[6,12,13,24,34-36] and the above falls into this range. A number of transition metal–thiourea complexes give a range of rotations (tilt) about the M–S bond of 30–57° and a range for the angle of twist of 14–35°.[6,12,34,35] This rotation (tilt) and twist occur regardless of the transition metal; *i.e.*, it occurs for Pt, Pd, Ni, Co, Fe, and Mn, and is independent of the coordination number of the metal [$Ni(tu)_6Br_2$, $Pd(tu)_4Cl_2$, $Pt(tu)_4Cl_2$, $Co(tu)_4Cl_2$], and is independent of anion [$Ni(tu)_6Br_2$, $Ni(tu)_6(NO_3)_2$,[37] $Ni(tu)_4Cl_2$]. Hence, we conclude that hydrogen bonding, van der Waals forces, and packing considerations do play a role in the precise orientation of the ligand; but, nevertheless, the rotation and twist are fundamental properties of the complex between the transition metal and thiourea.

---

(31) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

(32) M. R. Truter, *Acta Cryst.*, **22**, 556 (1967).

(33) M. M. Elcombe and J. C. Taylor, *ibid.*, **A24**, 410 (1968).

(34) G. F. Gasparri, A. Mangia, A. Musatti, and M. Nardelli, *ibid.*, **B25**, 203 (1969).

(35) M. Nardelli, G. F. Gasparri, G. G. Battistini, and P. Domiano, *ibid.*, **20**, 349 (1969).

(36) R. L. Girling and E. L. Amma, to be submitted for publication.

(37) E. L. Amma, unpublished results.

TABLE V

Rms Displacements along Principal Axes, Å

Atom	Axis 1	Axis 2	Axis 3
Pd	0.123 (1)	0.139 (1)	0.169 (1)
S(1)	0.142 (5)	0.158 (5)	0.195 (4)
S(2)	0.137 (5)	0.168 (5)	0.267 (4)
S(3)	0.133 (5)	0.148 (5)	0.222 (4)
S(4)	0.146 (5)	0.151 (4)	0.184 (4)
Cl(1)	0.167 (4)	0.197 (4)	0.247 (4)
Cl(2)	0.182 (4)	0.203 (4)	0.234 (4)
C(1)	0.122 (22)	0.149 (19)	0.192 (14)
N(1)	0.158 (15)	0.177 (15)	0.202 (14)
N(2)	0.152 (17)	0.169 (14)	0.239 (15)
C(2)	0.126 (21)	0.183 (19)	0.222 (14)
N(3)	0.182 (15)	0.209 (15)	0.237 (14)
N(4)	0.135 (18)	0.242 (15)	0.294 (15)
C(3)	0.131 (22)	0.154 (17)	0.219 (14)
N(5)	0.168 (15)	0.172 (15)	0.221 (12)
N(6)	0.133 (16)	0.179 (17)	0.245 (12)
C(4)	0.137 (21)	0.178 (17)	0.183 (14)
N(7)	0.128 (18)	0.186 (14)	0.233 (15)
N(8)	0.145 (16)	0.168 (16)	0.228 (14)

Equations of Least-Squares Planes of the Type[a] $Ax + By + Cz - D = 0$

	Plane no.				
	1	2	3	4	5
A	0.9019	−0.3305	−0.1297	0.9294	0.2312
B	0.1497	−0.8118	−0.9356	0.0967	0.6706
C	−0.4051	−0.4813	−0.3283	−0.3562	−0.7049
D	−0.4901	−0.6073	0.7804	−2.3069	−0.2906

Deviation of Atoms from the Least-Squares Planes, Å

	Plane no.					
	1	2	3	4		5
S(I)	−0.005 (2)	−0.004 (2)	0.001 (2)	0.008 (2)	Pd	0.0182 (3)
C(I)	0.018 (7)	0.013 (7)	−0.002 (7)	−0.028 (8)	S(1)	−0.095 (2)
N(2I-1)	−0.007 (7)	−0.005 (7)	0.001 (7)	0.010 (7)	S(2)	0.084 (2)
N(2I)	−0.006 (8)	−0.005 (8)	0.001 (7)	0.010 (7)	S(3)	0.083 (2)
					S(4)	−0.091 (2)

[a] *x, y, and z* refer to atom positional parameters in ångströms. All atoms are equally weighted in each least-squares plane.

Electron-pair repulsions between the electrons in the sulfur sp^2 lone-pair orbitals would make a lone-pair orbital–S–C angle less than 120°. The range of M–S–C angles of 106–116° makes it inescapable that thiourea is using an sp^2 lone-pair orbital in bonding to the metal. This M–S–C angle probably varies somewhat due to packing, hydrogen bonding, and nature of the metal. However, there is no obvious reason why a $M(tu)_4^{2+}$ molecule could not be completely planar including C, N, and H atoms. If such a hypothetical planar model is constructed with reasonable bonded distances and an M–S–C angle of 114°, no unreasonably short nonbonded distances can be found. Hence, there is no steric inhibition against such a planar model.

A "naive" Huckel π-electron calculation[38] for thiourea gives energies and symmetries of the π molecular orbitals (MO's) as follows: a_1, -2.23β; b_1, -1.50β; a_1', -0.81β; a_1'', $+1.03\beta$. The six π electrons, one from C and S and two from each nitrogen, fill these levels through a_1'; the next level is a strongly antibonding a_1''. It is well accepted that the π^* MO's of carbon monoxide and other such ligands are important in the stabilization of metal carbonyls and other complexes by behaving as π^* acceptors for metal electrons. The a_1'' MO of thiourea could fulfill this same function if the entire $M(tu)_4^{2+}$ unit were planar. However, this interaction is energetically expensive and the system has an energetically cheaper option open to it. If the π electrons are taken out of possible overlap with the d_{xz} and d_{yz} (e_g) metal orbitals by suitable rotation and twisting, then low-energy sulfur d orbitals that do not mix with the thiourea π orbitals are available as acceptors for metal electrons. We postulate that this electronic factor is the fundamental reason for the orientation of the thiourea molecules in transition metal–thiourea complexes and may well significantly influence the magnetic and spectral properties of such complexes.

Acknowledgment.—This project was supported by NIH Grant No. GM-13985.

---

[38] B. M. Gimarc, personal communication, University of South Carolina.