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Refinement of the Crystal Structure of the Charge Transfer Compound Pyridine—Iodomonochloride

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The crystal structure of the charge transfer complex of pyridine and iodomonochloride has been refined by three-dimensional X-ray methods using 884 observed reflections collected by counter methods. The geometry of the complex as found in an earlier investigation has been verified; the accuracy in bond length measurements is improved by a factor of ten relative to the earlier results.

The compound is planar with a linear N – I – Cl arrangement. The N – I and I – Cl bond lengths are 2.29 Å and 2.510 Å, respectively.

The majority of crystal structure determinations of charge transfer complexes between *n*-donor molecules and halogen or organic halides have been based on two-dimensional X-ray data. The crystal parameters of the heavy halogen atoms have usually been measured with fair accuracy; the positions of the atoms in the donor molecule were often more uncertain. Even if the general geometry of such complexes is quite well known,[1] the separation of the electron donor-electron acceptor atoms has in most cases been measured with uncertainties of the order 0.1 Å.

The charge transfer complex formed by pyridine and iodomonochloride [2] is one of the more stable addition compounds of this type. It was therefore selected as possibly suited for a reexamination by improved experimental methods.

EXPERIMENTAL. STRUCTURE REFINEMENT

Solutions of equimolecular amounts of pyridine and iodomonochloride in carbon tetrachloride were mixed. The yellow precipitate of the complex was dissolved in hot methanol; on slow cooling needle-formed crystals separated.

Unit cell parameters were determined from diffractometer measurements. The crystal data for the pyridine-ICl complex, C_5H_5NICl, mol. wt. 241.5 are: Monoclinic; $a = 4.274$ (0.002) Å; $b = 12.319$ (0.004) Å; $c = 14.094$ (0.004) Å;

$\beta = 94.99$ (0.02)° (figures in parentheses are estimated standard deviations); $V = 739.3$ Å^3; $Z = 4$; calculated density 2.17 g cm^{-3}; $F(000) = 448$; $\mu = 4.64$ mm^{-1}; space group $P2_1/c$.

Three-dimensional intensity data were recorded with the use of an automatic Picker diffractometer. The radiation was Nb-filtered Mo$K\alpha$ and the take-off angle 4°. The crystal had dimensions $0.08 \times 0.08 \times 0.2$ mm^3 and was mounted with the needle-axis (a) along the diffractometer ϕ-axis. The $\omega - 2\theta$ scanning mode was employed, the 2θ scan speed being 2° min^{-1} through the scan range from 1.2° below $2\theta(\alpha_1)$ to 1.2° above $2\theta(\alpha_2)$. Background counts were taken for 40 sec at each of the scan range limits.

The intensities of two standard reflections measured for every 50 reflections showed a decrease of 20 % during the three days of data collection. The data were adjusted according to this decrease and the estimated standard deviation of the intensities was taken as the square root of the total counts with a 5 % addition for the uncertainty in the adjustments.

Out of the 1417 reflections which were measured, 884 had intensities larger than twice the estimated standard deviation. These were regarded as "observed" whereas the remaining reflections were excluded from the refinement calculations.

The intensity data were corrected for Lorentz, polarization and absorption effects.

Atomic form factors used were those of Hanson *et al.*[3] for all atoms.

Computer programs employed in the structure determination are described in Ref. 4.

The coordinates for iodine and chlorine atoms given by Hassel and Rømming[2] formed the basis for the calculation of a three-dimensional Fourier map. From this all other non-hydrogen atoms were localized, and the refinement of the parameters proceeded by least-squares methods. Anisotropic thermal parameters were introduced, and in the final refinement stages hydrogen atoms in calculated positions (C – H distance 1.04 Å) were also taken into account. The hydrogen atomic parameters were not refined, however. The R-factor converged during the refinements to the value 0.065.

Inspection of the observed and calculated structure factors revealed that for low scattering angles the observed values were consistently higher than the calculated ones. This may be caused by too low background counts at the lower 2θ scan limit, which may happen at low scattering angles if the cut-off in intensity due to the β-filter falls within the scan range. Least-squares refinement with the omission of the 75 reflections with $\sin\theta/\lambda$ less than 0.2 resulted in the final R-value of 0.056. The weighted R-factor is 0.057. The procedure lowered the standard deviations in the parameters by 10 – 20 %.

A comparison of observed and calculated structure factors is given in Table 1; the final parameters for non-hydrogen atoms are listed in Table 2 the temperature factor being on the form $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Magnitudes and directions of the ellipsoids of thermal vibration are given in Table 3. No rigid-body corrections due to librational thermal motion was applied.

Table 1. Observed and calculated structure factors. The columns are h, k, l, $10\times|F|_o$ and $10\times F_c$.

0	0	2	409	- 348	0	8	1	100	71	1	9	-9	338	- 345	1	5	14	142	- 120	1	1	15	270	- 300	2	3	-10	184	- 181
0	0	4	1010	- 928	0	8	2	403	388	1	9	-8	132	110	1	4	13	360	- 367	1	0	14	247	- 301	2	3	-11	157	137
0	0	6	703	701	0	8	3	118	124	1	9	-6	298	301	1	4	11	220	211	1	0	12	352	353	2	3	-12	344	360
0	0	8	422	427	0	8	4	468	455	1	9	-5	458	443	1	4	10	128	- 100	1	0	10	254	258	2	3	-16	273	- 251
0	0	10	922	- 927	0	8	5	351	- 343	1	9	-4	455	- 444	1	4	9	455	440	1	0	8	1106	-1111	2	4	-15	286	- 248
0	0	12	163	168	0	8	6	448	- 453	1	9	-3	208	- 224	1	4	8	105	103	1	0	6	565	556	2	4	-13	231	265
0	0	14	295	310	0	8	7	155	165	1	9	-1	382	- 384	1	4	7	657	- 659	1	0	4	803	750	2	4	-11	162	164
0	0	16	203	- 228	0	8	9	141	135	1	9	0	553	556	1	4	6	211	- 221	1	0	2	456	- 416	2	4	-9	759	- 795
0	1	17	233	- 217	0	8	10	534	532	1	9	1	440	443	1	4	5	527	- 529	1	0	0	211	- 167	2	4	-7	234	227
0	1	14	171	- 140	0	8	14	158	- 175	1	9	2	109	- 118	1	4	4	122	- 130	1	0	-2	3100	2615	2	4	-6	146	137
0	1	13	305	300	0	9	13	153	- 153	1	9	4	146	- 119	1	4	3	1719	1766	1	0	-4	1117	-1044	2	4	-5	686	684
0	1	12	313	314	0	9	12	230	- 218	1	9	5	495	- 497	1	4	2	103	128	1	0	-6	925	- 919	2	4	-4	257	- 238
0	1	11	315	- 296	0	9	11	146	127	1	9	6	113	100	1	4	1	566	- 595	1	0	-8	667	693	2	4	-3	474	- 481
0	1	9	758	- 745	0	9	9	293	283	1	9	7	287	277	1	4	0	238	246	1	0	-10	241	255	2	4	-1	432	- 452
0	1	8	458	- 465	0	9	8	250	240	1	9	9	138	146	1	4	-1	502	- 518	1	0	-12	594	- 627	2	4	0	149	164
0	1	7	1209	1195	0	9	7	462	- 452	1	9	10	270	- 273	1	4	-2	427	- 417	1	0	-16	225	240	2	4	1	1393	1534
0	1	5	207	- 185	0	9	6	179	- 176	1	9	11	167	- 159	1	4	-3	965	956	2	0	-14	320	- 340	2	4	3	285	- 304
0	1	4	468	423	0	9	4	298	- 265	1	9	12	169	133	1	4	-5	559	573	2	0	-12	168	151	2	4	5	532	- 544
0	1	3	1609	-1415	0	9	3	510	491	1	9	12	205	- 195	1	4	-7	1144	-1181	2	0	-10	539	564	2	4	6	115	105
0	1	2	721	- 617	0	9	2	399	387	1	8	8	623	596	1	4	-9	267	263	2	0	-8	549	- 560	2	4	7	386	362
0	1	1	1008	853	0	9	1	398	- 384	1	8	6	314	- 294	1	4	-11	322	355	2	0	-6	624	- 620	2	4	8	133	- 101
0	2	0	926	788	0	10	0	280	- 288	1	8	5	109	101	1	4	-13	366	- 403	2	0	-4	1498	1365	2	4	9	205	220
0	2	1	898	- 775	0	10	1	367	352	1	8	4	497	- 487	1	3	-16	199	188	2	0	-2	730	- 663	2	4	11	440	- 423
0	2	2	1310	-1117	0	10	2	130	122	1	8	3	354	- 373	1	3	-14	416	- 441	2	0	0	824	- 731	2	5	12	154	- 124
0	2	3	976	- 855	0	10	3	335	313	1	8	2	482	490	1	3	-10	559	599	2	0	2	728	659	2	5	10	278	- 277
0	2	4	562	- 527	0	10	4	222	240	1	8	1	156	149	1	3	-9	270	283	2	0	4	545	517	2	5	9	205	- 199
0	2	5	1535	1446	0	10	5	616	- 592	1	8	0	369	383	1	3	-8	315	- 333	2	0	6	1218	-1171	2	5	8	503	500
0	2	6	705	679	0	10	6	170	- 190	1	8	-1	109	97	1	3	-6	986	- 965	2	0	8	249	250	2	5	7	188	168
0	2	7	377	- 377	0	10	7	212	203	1	8	-2	1009	-1017	1	3	-5	403	- 388	2	0	10	410	401	2	5	5	235	250
0	2	8	358	350	0	10	9	211	216	1	8	-4	355	359	1	3	-4	1361	1351	2	0	12	273	- 275	2	5	4	572	- 592
0	2	9	439	- 437	0	10	11	210	- 205	1	8	-6	454	455	1	3	-3	196	172	2	1	15	176	142	2	5	3	524	- 567
0	2	10	491	- 496	0	11	8	291	286	1	8	-7	176	200	1	3	-1	420	409	2	1	13	326	- 327	2	5	2	414	445
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0	2	12	155	181	0	11	4	419	- 394	1	8	-9	150	- 179	1	3	1	318	- 332	2	1	9	411	403	2	5	-1	451	484
0	2	14	269	235	0	11	2	490	473	1	8	-10	128	- 101	1	3	2	997	1032	2	1	8	340	326	2	5	-2	762	- 802
0	2	15	267	- 248	0	11	1	126	125	1	8	-12	310	331	1	3	3	149	- 156	2	1	7	376	- 347	2	5	-3	346	- 353
0	2	16	169	- 163	0	12	0	210	224	1	7	-11	342	352	1	3	4	792	793	2	1	6	183	- 163	2	5	-4	138	- 130
0	3	14	272	- 275	0	12	1	304	287	1	7	-10	122	145	1	3	5	271	272	2	1	5	564	- 541	2	5	-6	729	734
0	3	13	173	173	0	12	2	175	- 157	1	7	-9	606	- 655	1	3	6	698	- 686	2	1	4	482	- 462	2	5	-7	365	387
0	3	12	568	559	0	12	3	171	179	1	7	-6	129	- 106	1	3	7	178	- 171	2	1	3	1123	1111	2	5	-8	523	- 542
0	3	10	175	- 207	0	12	5	413	- 398	1	7	-5	613	632	1	3	8	123	- 133	2	1	2	257	250	2	5	-10	229	- 245
0	3	8	716	- 706	0	12	9	148	179	1	7	-3	575	- 585	1	3	10	685	670	2	1	1	111	- 110	2	5	-11	300	- 277
0	3	7	416	395	0	12	10	168	- 105	1	7	-1	745	- 742	1	3	11	206	202	2	1	0	178	191	2	5	-12	252	270
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0	3	5	146	- 154	0	13	3	281	- 253	1	7	1	860	892	1	3	16	179	161	2	1	-2	550	- 504	2	6	-14	246	234
0	3	4	1286	1183	0	13	2	271	267	1	7	5	870	- 866	1	2	13	325	- 335	2	1	-3	969	851	2	6	-10	280	- 313
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0	4	0	383	- 350	0	15	1	206	138	1	6	12	243	- 236	1	2	9	431	407	2	1	-8	220	- 240	2	6	-6	325	320
0	4	1	899	- 841	1	14	2	197	- 158	1	6	10	172	- 184	1	2	8	632	- 603	2	1	-11	558	602	2	6	-5	317	323
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0	4	4	91	- 93	1	13	-5	220	- 178	1	6	7	277	- 291	1	2	5	571	- 545	2	2	-14	239	- 248	2	6	-1	304	- 319
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0	4	9	532	- 525	1	13	2	141	- 129	1	6	2	533	555	1	2	0	1138	-1152	2	2	-8	400	- 399	2	6	4	404	- 411
0	4	11	500	507	1	13	5	237	244	1	6	1	300	- 325	1	2	-1	1011	-1010	2	2	-7	295	290	2	6	5	262	- 254
0	4	13	162	158	1	13	6	160	148	1	6	0	545	574	1	2	-2	1295	1220	2	2	-6	360	- 346	2	6	6	665	664
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0	5	12	463	473	1	12	7	176	191	1	6	-4	588	587	1	2	-6	550	- 455	2	2	-2	327	- 304	2	6	11	185	- 144
0	5	9	266	269	1	12	3	411	- 398	1	6	-5	160	169	1	2	-7	1008	-1024	2	2	-1	812	- 851	2	6	12	100	153
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0	5	6	303	306	1	12	-2	177	197	1	6	-8	472	- 483	1	2	-10	150	181	2	2	2	317	311	2	7	7	236	246
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0	5	1	256	- 264	1	11	-4	460	- 462	1	5	-16	195	156	1	1	-15	246	240	2	2	7	353	348	2	7	-1	725	772
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0	6	1	417	- 406	1	11	2	371	- 381	1	5	-11	213	223	1	1	-11	491	- 531	2	2	9	233	244	2	7	-3	615	- 619
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0	6	3	219	- 220	1	11	6	309	303	1	5	-9	424	- 461	1	1	-9	874	- 929	2	2	11	359	- 364	2	7	-7	471	493
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0	6	5	662	642	1	10	11	165	- 128	1	5	-6	628	- 633	1	1	-6	194	- 203	2	3	14	151	152	2	7	-13	231	247
0	6	6	492	- 476	1	10	9	201	- 224	1	5	-5	588	582	1	1	-5	1062	-1015	2	3	13	150	- 99	2	8	-10	346	- 349
0	6	7	215	- 212	1	10	7	279	251	1	5	-4	1135	1129	1	1	-4	873	787	2	3	12	202	- 185	2	8	-8	307	305
0	6	8	362	- 346	1	10	5	241	232	1	5	-3	144	- 153	1	1	-3	709	654	2	3	10	390	- 359	2	8	-7	130	- 103
0	6	9	379	- 371	1	10	4	146	- 142	1	5	-1	370	- 376	1	1	-2	208	- 176	2	3	9	174	142	2	8	-6	246	265
0	6	10	551	530	1	10	3	625	- 621	1	5	0	1105	-1144	1	1	-1	1034	945	2	3	8	768	731	2	8	-5	725	- 728
0	6	11	205	177	1	10	2	218	220	1	5	1	640	658	1	1	0	799	- 833	2	3	5	198	- 201	2	8	-3	141	119
0	6	12	137	- 135	1	10	1	318	329	1	5	2	563	580	1	1	1	1506	-1524	2	3	4	694	- 728	2	8	-2	231	250
0	6	14	232	- 205	1	10	0	116	82	1	5	3	122	129	1	1	2	472	452	2	3	3	299	314	2	8	0	448	467
0	7	13	202	- 231	1	10	-1	333	319	1	5	4	403	399	1	1	3	140	- 109	2	3	2	709	747	2	8	1	278	- 287
0	7	11	159	152	1	10	-2	256	- 244	1	5	5	523	- 522	1	1	4	199	202	2	3	0	666	747	2	8	2	340	- 347
0	7	9	459	442	1	10	-3	365	- 364	1	5	6	697	- 678	1	1	5	1430	1359	2	3	-1	226	- 242	2	8	4	307	- 321
0	7	7	867	- 841	1	10	-5	234	- 253	1	5	7	344	327	1	1	6	532	- 531	2	3	-2	919	- 955	2	8	6	528	529
0	7	4	109	119	1	10	-6	172	184	1	5	8	167	- 147	1	1	7	749	- 735	2	3	-3	238	229	2	8	10	231	- 208
0	7	3	791	753	1	10	-7	470	471	1	5	9	121	111	1	1	8	117	- 112	2	3	-4	88	- 83	2	8	12	222	170
0	7	2	202	- 194	1	10	-8	149	- 181	1	5	10	556	544	1	1	9	384	- 369	2	3	-6	966	948	2	9	10	180	113
0	7	1	719	- 713	1	9	-11	225	217	1	5	11	217	- 212	1	1	10	430	433	2	3	-7	336	- 320	2	9	9	182	- 167
0	8	0	1144	-1117	1	9	-10	160	- 213	1	5	12	264	- 261	1	1	11	340	346	2	3	-8	608	- 611	2	9	8	279	- 270

Table 1. Continued.

2	9	7	167	150
2	9	5	214	213
2	9	4	332	361
2	9	3	477	-470
2	9	-1	442	437
2	9	-2	414	409
2	9	-3	268	-272
2	9	-6	342	-348
2	9	-7	303	308
2	9	-8	198	204
2	9	-11	286	-238
2	9	-12	190	-136
2	10	-9	324	323
2	10	-8	171	148
2	10	-7	151	-142
2	10	-5	316	-324
2	10	-4	210	-179
2	10	-3	237	220
2	10	-1	261	258
2	10	0	185	168
2	10	1	521	-532
2	10	2	130	-142
2	10	3	223	195
2	10	5	216	253
2	11	8	262	-263
2	11	4	277	264
2	11	2	303	-290
2	11	0	227	-236
2	11	-2	370	387
2	11	-6	339	-366
2	11	-8	258	243
2	12	-5	221	-206
2	12	-3	157	206
2	12	-1	187	156
2	12	1	358	-354
2	12	5	179	169
2	13	4	181	136
2	13	3	258	210
2	13	2	208	-113
2	13	-1	218	-210
2	13	-3	162	152
3	12	-1	216	-249
3	11	-4	290	257
3	11	0	183	-208
3	11	2	250	241
3	10	3	199	204
3	10	-1	396	-397
3	10	-2	169	127
3	10	-3	144	157
3	10	-6	169	-111
3	10	-7	189	-204
3	9	-9	190	187
3	9	-8	229	-229
3	9	-5	231	-211
3	9	-4	228	247
3	9	-3	328	335
3	9	0	166	-176
3	9	1	297	-329
3	9	2	226	254
3	9	3	157	129
3	9	6	206	-202
3	9	7	166	-146
3	8	8	217	-208
3	8	4	432	453
3	8	2	201	-214
3	8	0	227	-249
3	8	-1	130	-159
3	8	-2	321	341
3	8	-6	436	-466
3	8	-10	170	161
3	7	-9	313	313
3	7	-5	409	-416
3	7	-3	510	529
3	7	1	432	-427
3	7	3	325	350
3	7	5	309	281
3	7	7	286	-267
3	6	10	180	136
3	6	8	168	-183
3	6	6	182	-136
3	6	4	436	464
3	6	3	173	-234
3	6	2	370	-394
3	6	0	313	-333
3	6	-1	330	343
3	6	-2	357	355
3	6	-3	212	-212
3	6	-4	173	185
3	6	-5	242	-227
3	6	-6	529	-515
3	6	-7	212	241
3	6	-8	227	207
3	6	-10	211	230
3	6	-11	185	-157
3	6	-12	208	-196
3	5	-13	227	-162
3	5	-10	306	-308
3	5	-9	243	250
3	5	-8	414	420
3	5	-5	259	-230
3	5	-4	469	-474
3	5	-3	363	370
3	5	-2	239	252
3	5	0	336	365
3	5	1	416	-464
3	5	2	443	-481
3	5	5	152	129
3	5	6	443	435
3	5	7	182	-182
3	5	8	224	-218
3	4	9	406	-401
3	4	7	215	219
3	4	5	281	298
3	4	3	389	-413
3	4	1	191	-205
3	4	-1	890	943
3	4	-3	397	-387
3	4	-5	412	-409
3	4	-7	459	440
3	4	-11	427	-412
3	3	-14	245	208
3	3	-12	152	-128
3	3	-10	350	-354
3	3	-9	211	-205
3	3	-8	638	623
3	3	-5	124	99
3	3	-4	709	-675
3	3	-3	236	-231
3	3	-2	322	331
3	3	0	510	570
3	3	1	262	277
3	3	2	561	-612
3	3	6	574	582
3	3	8	274	-249
3	3	10	161	-163
3	3	11	162	-115
3	2	10	171	-155
3	2	9	354	-328
3	2	8	259	236
3	2	7	243	240
3	2	6	188	178
3	2	5	270	267
3	2	4	459	-478
3	2	3	377	-385
3	2	2	304	307
3	2	1	292	-308
3	2	0	303	341
3	2	-1	645	693
3	2	-2	322	-315
3	2	-3	450	-406
3	2	-4	160	-136
3	2	-5	362	-329
3	2	-6	553	504
3	2	-7	432	408
3	2	-8	245	-237
3	2	-9	134	129
3	2	-10	275	-258
3	2	-11	354	-338
3	1	-13	290	326
3	1	-10	226	-194
3	1	-9	410	-402
3	1	-8	278	239
3	1	-7	302	267
3	1	-5	695	598
3	1	-4	312	-286
3	1	-3	892	-761
3	1	-2	207	174
3	1	0	203	240
3	1	1	673	736
3	1	2	325	-315
3	1	3	369	-377
3	1	4	112	-82
3	1	5	328	-340
3	1	6	224	221
3	1	7	374	374
3	1	11	270	-293
3	0	12	171	-109
3	0	10	223	-211
3	0	8	303	315
3	0	6	145	142
3	0	4	979	-926
3	0	2	456	429
3	0	0	405	369
3	0	-2	788	-706
3	0	-4	354	-336
3	0	-6	933	839
3	0	-8	327	-298
3	0	-10	349	-320
3	0	-12	394	376
4	0	-12	201	-166
4	0	-8	485	450
4	0	-4	478	-418
4	0	-2	264	244
4	0	0	269	260
4	0	2	615	-579
4	0	6	247	231
4	1	9	254	-233
4	1	5	256	277
4	1	4	172	182
4	1	3	282	-280
4	1	1	195	-210
4	1	0	189	-176
4	1	-1	453	452
4	1	-2	228	189
4	1	-5	466	-429
4	1	-6	260	-216
4	1	-7	370	345
4	1	-11	259	-234
4	2	-10	173	-123
4	2	-9	233	231
4	2	-8	221	254
4	2	-7	223	-194
4	2	-5	246	-202
4	2	-4	272	-239
4	2	-3	469	433
4	2	-2	235	230
4	2	-1	135	-120
4	2	0	166	226
4	2	1	219	-247
4	2	2	306	-337
4	2	3	169	201
4	2	5	203	199
4	2	7	233	-238
4	3	6	177	-169
4	3	4	351	370
4	3	0	371	-436
4	3	-2	319	340
4	3	-4	183	162
4	3	-5	137	-149
4	3	-6	375	-358
4	3	-10	336	320
4	4	-9	280	285
4	4	-7	203	-238
4	4	-5	214	-233
4	4	-3	481	512
4	4	-1	135	-135
4	4	1	265	-325
4	4	3	141	191
4	4	7	335	-319
4	5	5	191	-166
4	5	4	299	311
4	5	0	251	-318
4	5	-1	224	-244
4	5	-2	250	284
4	5	-5	250	235
4	5	-6	240	-279
4	5	-7	150	-137
4	5	-10	187	236
4	6	-8	281	-264
4	6	-7	158	-134
4	6	-4	234	252
4	6	-3	183	200
4	6	0	203	-218
4	6	2	269	301
4	7	5	222	-189
4	7	3	193	240
4	7	1	156	193
4	7	-1	251	-307
4	7	-5	352	308
4	7	-7	225	-245
4	8	-2	187	-176
4	8	2	295	319
4	9	0	169	140
4	9	-1	212	-190
5	4	-1	197	-203
5	3	-2	238	-253
5	2	0	193	-188
5	2	-5	214	218
5	1	-3	308	246
5	1	1	208	-182
5	1	2	169	122
5	0	0	351	-320
5	0	-2	223	159
5	0	-4	196	159
5	0	-6	246	-228

Table 2. Fractional atomic coordinates and thermal parameters ($\times 10^4$).

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	2938	681	1501	514	65	52	1	57	−1
	2	1	1	6	1	1	4	2	1
Cl	4943	−737	2680	809	84	67	19	14	44
	10	3	3	26	3	2	18	13	5
N	1199	1966	405	622	64	48	6	23	−2
	26	9	8	73	9	7	47	37	14
C1	−467	2827	682	673	68	61	−19	32	−17
	34	13	10	99	11	9	62	56	18
C2	−1549	3615	53	833	66	95	63	34	−1
	40	13	14	127	13	14	64	65	22
C3	−860	3484	−896	1318	80	68	−124	−68	34
	51	14	13	167	15	12	84	73	21
C4	734	2606	−1178	1109	94	59	−56	26	−29
	46	15	12	147	16	10	78	63	22
C5	1690	1852	−489	735	76	67	2	65	−8
	36	13	12	105	12	11	62	53	19

DISCUSSION

Bond lengths and angles are listed in Table 4 and in Fig. 1. Standard deviations were calculated from the correlation matrix ignoring standard deviations in cell parameters.

The complex is planar; none of the atoms deviates by more than the

Table 3. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and B-values along the principal axes of vibration given by the components of a unit vector **e** in fractional coordinates ($\times 10^3$).

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
I	.233	4.29	126	−7	63
	.223	3.92	22	81	3
	.210	3.49	−197	5	33
Cl	.293	6.76	−33	54	51
	.274	5.91	229	18	5
	.215	3.64	40	58	49
N	.240	4.54	2304	9	−5
	.222	3.88	40	−73	30
	.218	3.74	22	35	65
C1	.255	5.14	64	−41	60
	.249	4.90	−222	1	17
	.219	3.79	41	170	35
C2	.308	7.48	4	3	−71
	.281	6.23	225	23	8
	.219	3.79	−66	78	
C3	.367	10.64	−209	23	20
	.263	5.48	108	43	54
	.221	3.85	3	65	−42
C4	.322	8.19	229	−17	2
	.281	6.24	35	67	−38
	.226	4.03	37	43	60
C5	.267	5.62	170	−15	52
	.253	5.05	157	35	−39
	.238	4.47	−42	72	30

Table 4. Bond lengths (Å) and angles (°). Estimated standard deviations (in parentheses) apply to the last significant digits.

Bond length		Angle	
I – Cl	2.510(4)	Cl – I – N	178.7(3)
I – N	2.29(1)	I – N – C1	119.7(9)
N – C1	1.35(2)	I – N – C5	120.5(10)
N – C5	1.30(2)	I – N – C3	179.9(7)
C1 – C2	1.37(2)	N – C1 – C2	122(1)
C2 – C3	1.40(3)	C1 – C2 – C3	117(2)
C3 – C4	1.37(2)	C2 – C3 – C4	122(2)
C4 – C5	1.38(2)	C3 – C4 – C5	117(2)
		C4 – C5 – N	123(1)
		C5 – N – C1	120(1)

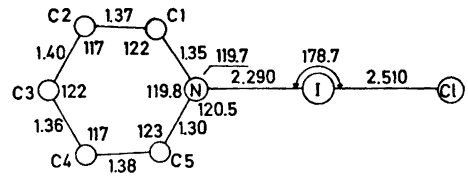

Fig. 1. Bond lengths (Å) and angles (°) in $C_5H_5N.ICl$.

standard deviation from a least squares plane through all non-hydrogen atoms. The pyridine part of the complex has dimensions in full agreement with those in pyridine itself;[5] if any distortion of the molecule has taken place by the complex formation, the accuracy of the present structure determination does not allow a demonstration of this.

The N – I – Cl arrangement is nearly linear, the angle being 179°. The line defined by the three atoms does also pass through the carbon atom opposite to the nitrogen atom. The complex seems indeed to possess a two-fold axis of symmetry through C3 – N – I – Cl.

The charge transfer bond length N – I of 2.29 Å and the I – Cl bond of 2.510 Å agree well with the results of the earlier investigation. The two bonds are 0.23 Å and 0.19 Å longer than the corresponding covalent radius sums, respectively. This corresponds to a very strong complex, and the relative bond lengths are in perfect agreement with those expected from the empirical rules reported for the bond lengths in charge transfer complexes in which iodine acts as the electron acceptor.[6]

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