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The Crystal Structure of Mercury(II) Cyanide–Silver Nitrate Dihydrate

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Mercury(II) cyanide–silver nitrate dihydrate, $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$, is monoclinic with $a = 16.74$ (3) Å, $b = 7.25$ (1) Å, $c = 10.62$ (2) Å, $\beta = 90.05$ (10)°, $Z = 6$, and space group C_2^3-$I2$. The measured and calculated densities are 3.5 (1) and 3.55 (1) g/cm^3, respectively. Visually estimated film intensity data for 1048 nonequivalent reflections were collected by Weissenberg and precession methods. The structure was refined by least squares to an R factor of 8.2%. Two sets of approximately linear chains, –Ag–NC–Hg–CN–Ag–, form the skeleton of the structure. (The orientation of the CN groups is assumed; it was not proven.) One type of chain linking mercury and silver atoms in special positions approximately coincides with the c axis. The other type forms crisscross chains linking mercury and silver atoms in general positions. The three Hg–C distances average 2.04 (8) Å and the three Ag–N distances average 2.11 (6) Å.

Introduction

The structure of $AgCN \cdot 2AgNO_3$ contains infinite chains of silver atoms bridged by disordered cyanides.[1] The structures of AgCN and AuCN are composed of parallel infinite chains of metal atoms presumably linked by disordered cyanides.[2] In view of these structures, it was felt that $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$, which was first discovered by Wohler in 1824,[3] might have infinite chains of alternating mercury and silver atoms bridged by ordered cyanide groups (with the carbon toward the mercury in light of the greater affinity of mercury for cyanide). The only previous X-ray crystallographic work appears to be a brief report[4] in which it was shown that the powder pattern of $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$ is distinct from that of a mixture of $Hg(CN)_2$ and $AgNO_3$.

Experimental Section

The compound was prepared by the method of Bougault and Cattelain.[5] Needlelike crystals suitable for diffraction purposes were prepared by recrystallization from water.

The unit cell dimensions and space group of $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$ were determined from Weissenberg and precession photographs with Mo Kα radiation (λ 0.7107 Å). The crystals are monoclinic; on the basis of systematic extinctions ($h + k + l = 2n + 1$), they belong to $I2$, Im, or $I2/m$. The spoon test for pyroelectricity[6] gave a positive result, which eliminates $I2/m$. The eventual solution of the structure showed the space group to be C_2^3–$I2$. The space group $I2$, rather than the conventional $C2$, was chosen so that β would be near 90°. The general equivalent positions in $I2$ are x, y, z; $\bar{x}, y, \bar{z}$; $^1/_2 + x, ^1/_2 + y, ^1/_2 + z$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$. The unit cell dimensions are $a = 16.74$ (3), $b = 7.25$ (1), $c = 10.62$ (2) Å, and $\beta = 90.05$ (10)°. The uncertainties are the 1 part in 600 we regard as the normal accuracy of the precession camera measurements.

The calculated density for six formula units per unit cell is 3.55 (1) g/cm^3. The density measured by flotation in a concentrated thallous formate–thallous malonate solution is 3.5 (1) g/cm^3. The density could not be measured accurately because the crystal slowly decomposed in the flotation solution. The value $Z = 6$ for $I2$ implies that at least two of the Hg atoms, two of the Ag atoms, and two of the NO_3 groups must be in special positions. All the other atoms could be in general positions. Multiple-film Weissenberg intensity data were collected for layers $h0l$ through $h8l$. Intensity data were also collected from $0kl$ and $hk0$ precession photographs, these data being used primarily for correlating the Weissenberg layers. All photographs were taken at room temperature with Mo Kα radiation. There were 1048 nonequivalent reflections of measurable intensity and another 682 reflections with intensities too weak to measure in the same region of reciprocal space; only the measurable reflections were used in the least-squares calculations.[7] A small, acicular crystal mounted so that the needle axis, b, was the oscillation axis was used for intensity data collection. The crystal had four lateral faces with approximate widths 0.044 mm for the 101 and $\bar{1}0\bar{1}$ faces and 0.036 mm for the $10\bar{1}$ and $\bar{1}01$ faces and a length of 4 mm. The linear absorption coefficient, μ, is 204 cm^{-1} for Mo Kα radiation. Absorption corrections as well as the usual Lorentz and polarization corrections were made.[8]

Structure Determination and Refinement

The mercury and silver positions were found from Patterson maps and confirmed on Fourier maps. Three-dimensional full-matrix least squares refinement of positional and anisotropic thermal parameters of only the heavy atoms converged to $R = 0.108$ and $r = 0.052$.[9] At this point the approximate positions of the light atoms could be determined from a difference Fourier map. In each cyanide group the height of the peak nearer the mercury was smaller than the height of the peak nearer the silver; this agrees with our preconceived

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(1) D. Britton and J. D. Dunitz, *Acta Crystallogr.*, **19**, 815 (1965).

(2) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, 1962, p 735.

(3) F. Wohler, *Ann. Phys. Chem.*, **1**, 231 (1824). It is of historical interest to note that in this paper, where Wohler reported the inadvertent preparation of $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$, he also reported for the first time the preparation of $AgCN \cdot 2AgNO_3$.

(4) P. Spacu, *C. R. Acad. Sci.*, **202**, 1987 (1936).

(5) J. Bougault and E. Cattelain, *Bull. Soc. Chim. Fr.*, [5] **2**, 996 (1935).

(6) C. W. Bunn, "Chemical Crystallography," 2nd ed, Oxford University Press, London, 1961, p 321.

(7) At the end of the eventual refinement about 10% of these unobserved reflections had calculated intensities larger than the minimum observed intensity, although in no case was the calculated intensity twice the minimum observed intensity. On reinspection of the films most of these reflections could be found as very weak spots. There were also 14 reflections with large calculated intensities that occurred at such low angles that they could not be recorded.

(8) Unless otherwise mentioned all calculations including the Weissenberg absorption corrections were made using programs supplied by Dr. L. W. Finger, formerly of the Geology Department, University of Minnesota. The absorption corrections for the precession data were made with a locally modified version of the program DATAP2: P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965); we thank Professor Coppens for providing a copy of this program. The group refinements were made using a local modification of an earlier modification by Doedens of the program ORFLS; we thank Professor J. A. Ibers for supplying this program. All computer calculations were made on the Control Data 1604 or 6600 computers of the University of Minnesota Computer Center.

(9) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$; the numerator of r was the function minimized; $w = 1$ for $F_o \leqslant 140$; $w = (140/F_o)^4$ for $F_o > 140$.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	L	FO	FC
*** K = 0 ***			
2	0	110	102
4	0	323	308
6	0	268	264
8	0	204	162
10	0	317	310
14	0	159	153
16	0	205	191
20	0	122	125
3	1	380	353
5	1	332	295
7	1	175	152
11	1	353	333
13	1	91	82
0	2	234	196
2	2	610	593
4	2	50	52
6	2	432	403
8	2	62	46
10	2	103	69
12	2	223	206
16	2	174	179
18	2	113	112
1	3	161	145
3	3	174	140
5	3	377	321
7	3	233	217
11	3	95	80
13	3	245	230
15	3	85	64
17	3	126	126
0	4	78	39
2	4	355	300
4	4	370	324
6	4	143	117
8	4	447	424
12	4	90	89
14	4	105	107
16	4	117	97
18	4	152	160
3	5	250	210
5	5	97	76
7	5	211	174
9	5	143	141
11	5	105	99
13	5	132	126
15	5	153	147
19	5	120	128
0	6	335	303
2	6	164	126
4	6	278	263
6	6	148	136
8	6	107	95
10	6	330	320
14	6	155	147
1	7	221	204
5	7	297	274
11	7	105	111
13	7	157	135
15	7	122	125
0	8	223	208
2	8	209	188
4	8	87	71
6	8	185	194
10	8	95	109
12	8	205	211
16	8	135	157
1	9	71	88
7	9	213	215
11	9	86	75
17	9	91	98
0	10	41	50
2	10	229	225
4	10	122	118
8	10	168	166
12	10	118	126
18	10	142	137
1	11	93	76
3	11	94	106
9	11	138	159
0	12	116	117
4	12	174	192
10	12	80	97
5	13	105	104
0	14	87	101
6	14	118	143
-3	1	128	119
-5	1	378	365
-7	1	65	59
-9	1	263	249
-11	1	76	69
-13	1	76	52
-15	1	111	113
-17	1	80	70
-19	1	113	127
-4	2	278	286
-6	2	186	165
-8	2	341	332
-10	2	145	143
-12	2	86	84
-14	2	267	256
-18	2	95	77
-3	3	507	620
-5	3	116	107
-7	3	119	113
-11	3	151	126
-13	3	164	172
-17	3	82	93
-19	3	100	78
-2	4	329	319
-6	4	301	305
-8	4	270	277
-12	4	230	250
-18	4	105	94
-1	5	406	402
-3	5	76	67
-7	5	109	119
-9	5	163	152
-11	5	163	181
-17	5	107	118
-19	5	81	44
-2	6	178	176
-4	6	156	141
-6	6	383	400
-10	6	150	153
-16	6	115	124
-3	7	90	83
-5	7	144	136
-7	7	96	110
-9	7	153	151
-15	7	107	109
-2	8	73	52
-4	8	290	291
-8	8	90	91
-10	8	94	90
-14	8	125	127
-1	9	114	105
-3	9	143	143
-7	9	76	75
-9	9	129	128
-11	9	75	37
-13	9	92	81
-2	10	212	224
-8	10	124	132
-12	10	124	135
-1	11	105	124
-3	11	76	58
-7	11	119	128
-2	12	79	81
-6	12	117	132
-10	12	99	79
-5	13	112	102
-4	14	110	109
*** K = 1 ***			
1	0	36	27
3	0	333	346
5	0	227	185
7	0	392	408
9	0	220	207
11	0	118	107
13	0	212	205
15	0	70	73
17	0	112	108
0	1	167	144
4	1	212	201
6	1	183	176
8	1	267	226
10	1	103	110
14	1	147	144
16	1	99	88
18	1	134	132
1	2	88	74
3	2	98	70
5	2	251	245
7	2	147	120
9	2	331	339
11	2	168	139
13	2	144	134
15	2	116	102
17	2	80	89
19	2	119	108
0	3	260	245
2	3	172	150
4	3	260	234
6	3	209	192
8	3	131	127
10	3	248	227
12	3	111	119
14	3	76	69
16	3	79	63
18	3	88	70
20	3	91	124
1	4	376	363
3	4	183	162
5	4	314	276
7	4	102	83
11	4	248	259
13	4	130	107
15	4	164	180
17	4	79	72
0	5	89	51
2	5	256	203
4	5	175	159
6	5	293	271
8	5	117	101
10	5	81	86
12	5	166	140
14	5	136	139
16	5	119	106
1	6	277	263
3	6	291	280
5	6	163	132
7	6	304	285
11	6	84	85
13	6	150	143
15	6	101	87
17	6	152	171
0	7	126	125
2	7	148	109
4	7	125	102
6	7	74	79
8	7	202	198
10	7	95	87
12	7	142	137
14	7	80	81
18	7	90	99
1	8	113	95
3	8	232	232
5	8	161	148
7	8	131	114
9	8	192	191
11	8	77	86
13	8	121	103
19	8	101	125
0	9	133	149
2	9	117	110
4	9	176	167
10	9	133	127
12	9	89	79
14	9	112	131
1	10	123	115
3	10	69	50
5	10	193	207
7	10	80	65
9	10	137	135
11	10	123	136
15	10	104	113
0	11	96	100
2	11	78	69
4	11	67	45
6	11	138	139
1	12	121	130
7	12	127	137
11	12	101	120
2	13	81	94
8	13	82	88
3	14	98	121
-4	1	177	190
-6	1	178	139
-8	1	151	124
-10	1	85	74
-12	1	223	232
-14	1	107	100
-16	1	93	78
-3	2	213	226
-5	2	263	290
-7	2	222	228
-9	2	112	109
-11	2	257	216
-15	2	61	47
-17	2	93	103
-2	3	198	220
-4	3	106	105
-6	3	199	189
-8	3	113	105
-10	3	228	215
-12	3	64	58
-16	3	93	93
-18	3	64	65
-1	4	268	253
-3	4	192	210
-5	4	285	306
-7	4	63	62
-9	4	187	176
-11	4	56	47
-13	4	73	61
-15	4	158	170
-2	5	83	84
-4	5	216	231
-6	5	121	122
-8	5	151	150
-10	5	62	61
-12	5	56	60
-14	5	130	119
-1	6	105	77
-3	6	230	249
-7	6	123	123
-9	6	142	145
-11	6	80	81
-13	6	173	179
-2	7	192	208
-4	7	85	73
-6	7	84	82
-8	7	140	125
-10	7	89	92
-12	7	127	103
-1	8	216	207
-5	8	62	49
-7	8	192	194
-9	8	82	85
-11	8	136	129
-13	8	66	49
-2	9	75	80
-6	9	127	122
-8	9	70	68
-10	9	78	63
-1	10	124	116
-3	10	75	64
-5	10	161	188
-7	10	82	69
-9	10	104	97
-11	10	83	86
-4	11	107	109
-1	12	77	59
-3	12	105	134
*** K = 2 ***			
0	0	350	387
2	0	412	390
4	0	247	239
6	0	271	260
8	0	109	102
10	0	292	288
12	0	153	144
14	0	117	117
16	0	90	97
18	0	98	100
20	0	95	111
3	1	97	101
5	1	222	211
7	1	142	119
9	1	225	217
11	1	202	201
13	1	106	96
15	1	129	109
17	1	107	91
2	2	270	255
4	2	411	400
6	2	274	269
8	2	88	81
10	2	69	56
12	2	237	238
14	2	131	118
16	2	128	130
18	2	69	62
20	2	83	79
1	3	109	96
3	3	277	245
5	3	74	59
7	3	317	296
9	3	101	92
11	3	102	90
13	3	110	111
15	3	147	134
17	3	136	128
0	4	123	122
2	4	222	207
4	4	236	227
6	4	318	299
8	4	225	247
10	4	149	140
12	4	123	108
14	4	157	143
16	4	90	74
18	4	116	124
20	4	78	75
1	5	230	221
3	5	152	143
5	5	110	86
9	5	270	254
11	5	76	72
13	5	137	113
17	5	97	104
0	6	272	270
2	6	120	96
4	6	268	247
6	6	148	142
8	6	171	167
10	6	162	175
12	6	157	157
14	6	129	117
16	6	92	64
20	6	97	104
1	7	160	158
3	7	201	195
5	7	176	173
7	7	65	64
11	7	181	180
13	7	69	98
15	7	113	118
0	8	137	126
2	8	140	132
4	8	90	85
6	8	215	212
8	8	101	84
10	8	122	119
12	8	89	100
14	8	154	138
16	8	92	102
1	9	146	132
3	9	77	78
5	9	88	92
7	9	134	135
9	9	101	105
11	9	79	71
13	9	95	80
0	10	159	153
2	10	145	146
4	10	104	99
6	10	88	85
8	10	155	166
10	10	106	71
12	10	104	109
1	11	68	44
3	11	149	140
9	11	97	94
0	12	110	95
2	12	99	101
4	12	123	130
5	13	123	118
-5	1	181	187
-7	1	275	277
-9	1	209	209
-15	1	156	155
-17	1	74	79
-2	2	132	141
-4	2	359	379
-6	2	130	127
-8	2	189	190
-10	2	153	149
-12	2	159	152
-14	2	142	150
-16	2	83	93
-18	2	84	92
-1	3	180	184
-3	3	176	195
-5	3	194	220
-7	3	181	178
-9	3	114	101
-13	3	191	192
-15	3	76	91
-2	4	358	394
-4	4	181	177
-6	4	127	131
-8	4	163	177
-10	4	194	197
-12	4	167	183
-14	4	64	47
-1	5	208	197
-5	5	92	80
-7	5	210	216
-9	5	63	72
-11	5	135	134
-13	5	70	63
-17	5	93	82
-2	6	171	156
-4	6	190	195
-6	6	181	186
-8	6	176	179
-10	6	144	149
-12	6	73	66
-16	6	94	105
-1	7	123	100
-5	7	216	217
-7	7	88	76
-9	7	64	65
-11	7	68	64
-15	7	96	91
-2	8	168	166
-4	8	145	156
-6	8	103	94
-8	8	99	101
-10	8	88	102
-12	8	92	56
-16	8	102	55
-3	9	153	163
-5	9	74	63
-7	9	82	65
-13	9	98	90
-2	10	154	160
-4	10	97	81
-8	10	88	116
-1	11	109	105
-7	11	97	92
-2	12	106	80
*** K = 3 ***			
1	0	256	257
3	0	252	224
5	0	298	318
7	0	92	97
9	0	133	123
11	0	153	144
13	0	168	157
15	0	142	141
17	0	116	104
0	1	169	163
4	1	164	164
6	1	160	165
8	1	264	266
10	1	104	96
12	1	99	90
14	1	94	94
16	1	140	142
18	1	85	64
1	2	309	300
3	2	258	238
5	2	166	163
7	2	262	260
9	2	130	105
11	2	194	168
13	2	70	64
15	2	83	76
17	2	112	103
19	2	116	110
0	3	336	320
2	3	234	212
4	3	89	74
8	3	148	132
10	3	220	216
12	3	116	113
14	3	132	126
16	3	68	53
18	3	103	103
1	4	142	129
3	4	310	281
5	4	242	228
7	4	143	144
9	4	179	169
11	4	126	121
13	4	192	197
0	5	208	197
2	5	223	201
4	5	195	189
6	5	167	169
8	5	100	96
10	5	65	66
12	5	142	145
14	5	112	102
16	5	133	140
1	6	143	124
3	6	54	45
5	6	227	215
7	6	172	168
9	6	153	141
11	6	136	145
13	6	75	86
15	6	139	156
19	6	72	68
0	7	144	139
2	7	185	172
4	7	143	132
6	7	132	125
8	7	165	158
10	7	141	137
18	7	110	124
1	8	194	199
3	8	107	93
5	8	103	95
7	8	135	134
9	8	119	114
11	8	122	122
13	8	105	115
0	9	95	81
2	9	127	127
4	9	147	141
6	9	78	65
8	9	109	102
10	9	118	112
12	9	119	119
1	10	101	101
3	10	145	151
5	10	121	118
7	10	128	125
0	11	96	75
4	11	98	82
6	11	109	112
10	11	96	92
5	12	103	94
9	12	105	110
-4	1	203	226
-6	1	260	293
-8	1	106	111
-10	1	144	139
-12	1	132	126
-14	1	117	120
-18	1	85	48
-1	2	192	193
-3	2	275	304
-5	2	76	77
-7	2	48	51
-9	2	180	181
-11	2	181	186
-13	2	107	108
-15	2	71	61
-2	3	153	157
-4	3	160	171
-6	3	178	187
-8	3	166	183
-10	3	116	111
-12	3	72	70
-14	3	76	53
-16	3	98	101
-1	4	225	231
-3	4	201	202
-5	4	156	181
-7	4	221	231
-9	4	169	176
-11	4	87	83
-13	4	102	111
-15	4	75	55
-17	4	99	103
-2	5	129	127
-4	5	179	171
-6	5	152	152
-8	5	64	68
-12	5	82	83
-14	5	128	132
-16	5	83	67
-1	6	222	214
-3	6	198	203
-5	6	196	188
-7	6	133	127
-9	6	78	87
-11	6	137	152
-13	6	84	67
-15	6	91	86
-2	7	162	154
-4	7	118	121
-8	7	118	121
-10	7	97	103
-12	7	133	124
-1	8	137	145
-3	8	146	131
-5	8	110	98
-7	8	68	76
-9	8	148	140
-4	9	70	75
-6	9	149	150
-8	9	103	85
-10	9	96	76
-1	10	111	106
-3	10	124	126
-5	10	88	81
-7	10	107	114
-2	11	98	84
-4	11	111	108
-1	12	115	112
*** K = 4 ***			
0	0	119	109
2	0	219	227
4	0	93	104
6	0	122	129
8	0	290	306
10	0	113	115
12	0	149	143
3	1	298	314
5	1	132	132
9	1	108	108
11	1	149	152
13	1	129	137
15	1	118	99
0	2	147	135
2	2	128	122
4	2	225	211
6	2	118	108
8	2	140	132
10	2	171	177
12	2	84	88
14	2	163	174
1	3	113	106
3	3	167	141
5	3	281	288
7	3	174	175
9	3	128	116
13	3	119	109
15	3	129	111
17	3	98	93
0	4	281	283
2	4	137	109
6	4	200	175
8	4	124	107
10	4	171	159
12	4	123	115
16	4	131	141
1	5	135	119
3	5	144	128
5	5	114	97
7	5	188	190
9	5	149	140
11	5	152	159
0	6	98	87
2	6	283	276
4	6	124	104
6	6	128	119
8	6	107	110
10	6	93	91
12	6	121	135
1	7	92	79
3	7	151	130
5	7	131	130
7	7	97	91
9	7	111	123
11	7	101	90
13	7	136	146
2	8	81	42
4	8	187	188
6	8	90	95
8	8	149	151
1	9	100	92
5	9	95	99
7	9	104	108
0	10	144	134
4	10	121	67
6	10	115	125
1	11	121	126
2	12	121	109
-3	1	67	69
-5	1	152	159
-7	1	144	144
-9	1	155	143
-11	1	123	122
-13	1	123	111
-15	1	89	72
-17	1	109	115
-19	1	105	60
-2	2	172	175
-6	2	282	300
-8	2	50	61
-10	2	55	62
-12	2	74	80
-16	2	95	121
-1	3	109	102
-3	3	141	146
-5	3	147	147
-7	3	118	107
-9	3	111	111
-11	3	156	167
-13	3	97	109
-15	3	86	89
-2	4	132	125
-4	4	183	192
-10	4	137	146
-12	4	73	73
-14	4	105	112
-1	5	178	170
-3	5	132	132
-5	5	125	122
-7	5	124	130
-9	5	157	181
-11	5	97	90
-2	6	122	113
-4	6	114	105
-6	6	70	45
-8	6	145	151
-10	6	84	49
-1	7	121	111
-3	7	145	155
-5	7	123	120
-7	7	96	115
-2	8	122	115
-4	8	84	58
-6	8	132	132
-1	9	160	148
-3	9	110	96
-5	9	104	81
-4	10	104	108
-6	10	104	95
*** K = 5 ***			
1	0	240	222
5	0	230	241
7	0	87	85
9	0	45	48
11	0	129	117
15	0	174	174
0	1	144	154
4	1	115	97
6	1	234	230
8	1	61	44
10	1	159	159
12	1	84	93
14	1	65	65
16	1	96	102
1	2	258	246
3	2	144	127
5	2	75	57
7	2	194	183
9	2	115	98
11	2	87	80
17	2	121	135
0	3	95	90
2	3	241	243
4	3	104	101
6	3	55	53
8	3	163	158
10	3	73	56
12	3	175	189
1	4	99	85
3	4	253	237
7	4	151	150
9	4	162	152
11	4	99	85
13	4	117	118
0	5	148	143
4	5	207	209
6	5	115	103
8	5	64	67
10	5	106	92
12	5	73	53
14	5	160	167
5	6	182	168
9	6	187	185
11	6	84	87
15	6	100	103
0	7	164	170
4	7	118	98
6	7	163	162
8	7	86	80
10	7	103	108
16	7	117	118
1	8	170	179
7	8	99	93
11	8	157	154
2	9	139	139
4	9	72	58
6	9	119	118
8	9	103	101
12	9	94	105
3	10	147	150
7	10	84	89
4	11	89	99
8	11	96	117
5	12	106	89
9	12	102	94
-4	1	240	266
-6	1	76	47
-8	1	92	90
-10	1	126	132
-12	1	99	96
-14	1	93	92
-1	2	97	93
-3	2	159	171
-5	2	34	47
-9	2	184	190
-13	2	130	133
-15	2	57	36
-2	3	196	222
-4	3	138	137
-6	3	44	51
-8	3	161	173
-10	3	95	98
-12	3	58	61
-14	3	63	63
-1	4	100	85
-3	4	101	95
-7	4	215	223
-11	4	110	96
-13	4	74	78
-2	5	177	181
-4	5	106	97
-6	5	144	150
-10	5	54	41
-12	5	115	118
-16	5	79	92
-1	6	181	185
-5	6	192	187
-11	6	112	110
-13	6	76	54
-15	6	80	66
-2	7	119	99
-4	7	120	112
-10	7	135	142
-3	8	135	124
-5	8	101	98
-9	8	98	101
-4	9	118	106
-8	9	124	118
-3	10	121	113
-7	10	104	93
-2	11	114	117
-6	11	97	87
-1	12	94	92
*** K = 6 ***			
0	0	78	81
2	0	182	197
4	0	77	55
6	0	94	68
8	0	169	183
10	0	87	64
12	0	130	111
3	1	250	239
7	1	73	68
9	1	149	167
11	1	66	47
13	1	159	152
0	2	90	95
2	2	95	64
4	2	205	213
8	2	125	101
10	2	128	100
12	2	100	81
14	2	146	124
1	3	132	102
5	3	222	214
9	3	125	118
11	3	107	99
15	3	115	136
0	4	199	174
6	4	162	159
10	4	170	144
12	4	63	44
1	5	203	211
7	5	169	153
11	5	128	134
0	6	113	63
2	6	197	178
4	6	107	45
8	6	131	105
12	6	176	133
3	7	168	168
7	7	160	125
9	7	87	93
4	8	151	132
5	9	142	124
-3	1	87	114
-7	1	180	227
-11	1	102	111
-2	2	134	116
-4	2	98	94
-6	2	163	187
-10	2	83	56
-12	2	90	88
-1	3	175	185
-3	3	103	62
-5	3	164	197
-11	3	106	130
-2	4	96	88
-4	4	159	151
-10	4	129	142
*** K = 7 ***			
5	0	145	155
9	0	94	84
11	0	91	67
13	0	87	77
15	0	83	76
4	1	37	47
6	1	148	161
8	1	72	70
1	2	108	104
3	2	71	57
5	2	85	64
7	2	111	106
11	2	105	118
0	1	211	155
0	3	77	63
2	3	175	171
6	3	86	83
8	3	143	124
10	3	80	80
12	3	94	93
3	4	151	148
5	4	81	76
7	4	87	56
9	4	94	58
4	5	152	137
8	5	128	130
5	6	137	121
7	6	106	84
0	7	134	140
6	7	106	93
10	7	107	124
1	8	103	89
2	9	133	125
-4	1	134	143
-6	1	68	52
-10	1	93	104
-1	2	89	79
-3	2	116	137
-5	2	64	35
-9	2	96	100
-2	3	100	96
-4	3	66	54
-8	3	131	148
-1	4	102	96
-3	4	102	91
-5	4	69	67
-7	4	97	96
-9	4	97	64
-2	5	121	110
-6	5	118	141
-1	6	107	106
-3	6	85	75
-5	6	102	76
-4	7	108	108
*** K = 8 ***			
4	0	52	37
6	0	64	45
8	0	71	82
10	0	76	69
12	0	84	84
3	1	123	121
5	1	54	49
7	1	71	74
9	1	109	105
11	1	63	79
0	2	58	55
2	2	102	84
4	2	137	143
6	2	70	79
1	3	68	55
3	3	73	69
5	3	98	99
7	3	79	62
9	3	82	97
11	3	74	57
13	3	80	68
0	4	89	87
2	4	48	31
4	4	73	61
6	4	108	106
8	4	89	80
10	4	74	78
1	5	139	139
7	5	77	67
9	5	76	68
0	6	73	70
2	6	71	79
4	6	74	45
8	6	64	68
10	6	107	71
12	6	101	82
7	7	62	79
-3	1	64	73
-5	1	87	86
-7	1	120	143
-9	1	68	74
-11	1	64	56
-2	2	37	58
-4	2	77	73
-6	2	76	92
-1	3	124	121
-3	3	84	99
-5	3	102	127
-7	3	45	42
-2	4	95	86
-4	4	74	85
-1	5	66	81
-3	5	90	81
-4	6	77	75

notion that the cyanide groups would be ordered in this compound but should not be regarded as proof. Since over 60% of the electrons in this compound are in the mercury and silver atoms, we did not expect to find the light-atom positions accurately. For this reason refinement was continued with the light atoms in the cyanide and nitrate groups treated as members of rigid groups. The group refinement with all atoms given isotropic temperature factors refined to $R = 0.113$ and $r = 0.051$. Further refinement with anisotropic temperature factors for the heavy atoms converged to a final $R = 0.082$ and $r = 0.043$. The standard deviations in the light-atom positions at this point made it clear that the group parameters used were more accurate than any parameters we might expect to find by allowing the light atoms to refine individually. Refinement was therefore concluded at this point. A difference Fourier map with these final parameters showed peaks approximately 4 e⁻/Å³ in the vicinity of the Hg and Ag positions and showed other peaks of the order of 2 e⁻/Å³; this was judged to be reasonable confirmation of the proposed structure.

The scattering factors used, including anomalous scattering coefficients for mercury and silver, were taken from ref 10. No extinction corrections were made since no trend of increasing $|F_c| - |F_o|$ with increasing $|F_o|$ was found.

The final F_o and F_c values, with absolute scaling, are listed in Table I. The final positional and thermal parameters are given in Tables II and III for the nongroup atoms and in Tables IV and V for the group atoms.

TABLE II

FINAL ATOMIC COORDINATES FOR NONGROUP ATOMS[a]

Atom	x	y	z	B,[b] Å²
Hg(1)	0	0	0	
Hg(2)	0.1972 (1)	0.4127 (5)	0.8490 (2)	
Ag(1)	0	0.0619 (13)	$^1/_2$	
Ag(2)	0.0665 (3)	0.6269 (10)	0.3922 (5)	
$H_2O(1)$	0.189 3)	0.215 (8)	0.223 (5)	4.6 (11)
$H_2O(2)$	0.158 (3)	0.612 (7)	0.201 (4)	3.2 (9)
$H_2O(3)$	0.108 (3)	0.295 (8)	0.438 (5)	4.4 (10)

[a] Estimated standard deviations (in parentheses) occur in the last digit. The y parameter of Hg(1) was arbitrarily fixed to define the origin. [b] Thermal parameters for Hg and Ag are found in Table III.

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(10) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Tables 3.3.1A, 3.3.1B, 3.3.2C.

TABLE III

ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	23 (1)	64 (8)	23 (3)	0	−5 (1)	0
Hg(2)	16 (1)	93 (5)	49 (2)	10 (2)	−10 (1)	12 (3)
Ag(1)	42 (3)	220 (21)	48 (6)	0	−5 (3)	0
Ag(2)	23 (2)	177 (13)	91 (5)	−12 (4)	−18 (3)	−27 (7)

[a] The anisotropic temperature factor has the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

TABLE IV

RIGID-BODY COORDINATES FOR GROUPS[a]

Group	x	y	z	δ	ϵ	η
$NO_3(1)$	0	0.480 (6)	0	0	0	0.08 (6)
$NO_3(2)$	0.200 (1)	0.932 (4)	0.912 (2)	3.20 (3)	3.24 (3)	2.69 (3)
CN(1)	−0.000 (3)	0.015 (9)	0.302 (4)	−3.1388	−3.09 (9)	−3.11 (7)
CN(2)	0.039 (3)	0.549 (9)	0.685 (5)	−0.39 (8)	2.9664	0.46 (6)
CN(3)	0.158 (3)	0.779 (9)	0.497 (5)	0.27 (11)	3.0444	0.60 (8)

[a] The origin of the group is on the nitrogen in each case. The angles are in radians. Values for which no error is indicated are nonrefineable. δ, ϵ, and η are angles that bring about alignment (except for translation) of an internal-coordinate system within the group with a fixed external system. See S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18,** 511 (1965), for the definitions.

TABLE V

POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR GROUP ATOMS

Group	Atom	x	y	z	B, Å^2
$NO_3(1)$	O(1)	0	0.649 (6)	0	2.7 (11)
	O(2)	0.063 (1)	0.396 (6)	0.007 (10)	6.6 (14)
	N(4)	0	0.480 (6)	0	0.4 (8)
$NO_3(2)$	O(3)	0.189 (2)	1.053 (5)	0.834 (3)	2.8 (8)
	O(4)	0.243 (2)	0.801 (5)	0.889 (4)	4.1 (10)
	O(5)	0.168 (3)	0.943 (6)	1.015 (3)	4.3 (10)
	N(5)	0.200 (1)	0.932 (4)	0.912 (2)	2.4 (8)
CN(1)	N(1)	−0.000 (3)	0.015 (9)	0.302 (4)	2.8 (8)
	C(1)	−0.003 (3)	0.007 (9)	0.193 (4)	2.7 (11)
CN(2)	N(2)	0.039 (3)	0.549 (9)	0.685 (5)	3.8 (11)
	C(2)	0.098 (3)	0.506 (9)	0.733 (5)	0.8 (6)
CN(3)	N(3)	0.158 (3)	0.779 (9)	0.497 (5)	3.0 (10)
	C(3)	0.212 (3)	0.822 (9)	0.559 (5)	3.3 (13)

TABLE VI

PRINCIPAL INTERATOMIC DISTANCES (Å)

Hg(1)–C(1)	2.05 (4)	Hg(2)–O(4)	2.95 (4)
Hg(1)–O(1)	2.55 (4)	Hg(2)–O(4)′	2.84 (4)
Hg(1)–O(2)	3.06 (4)	Ag(1)–N(1)	2.13 (4)
Hg(1)–O(5)	2.85 (4)	Ag(1)–$H_2O(3)$	2.57 (6)
Hg(2)–C(2)	2.16 (5)	Ag(2)–N(2)	2.02 (5)
Hg(2)–C(3)	1.92 (5)	Ag(2)–N(3)	2.18 (6)
Hg(2)–O(2)	2.82 (7)	Ag(2)–$H_2O(2)$	2.56 (5)
Hg(2)–O(3)	2.62 (4)	Ag(2)–$H_2O(3)$	2.55 (6)
Hg(2)–O(3)′	2.92 (4)	$H_2O(1)$–$H_2O(2)$	2.77 (7)
		$H_2O(1)$–$H_2O(3)$	2.73 (8)

TABLE VII

PRINCIPAL INTERATOMIC ANGLES (DEG)

Hg(1)–C(1)–N(1)	177 (5)	O(2)–Hg(2)–O(3)	87 (1)
C(1)–Hg(1)–C(1)	177 (4)	O(2)–Hg(2)–O(4)	99 (1)
O(1)–Hg(1)–C(1)	91 (2)	O(3)–Hg(2)–O(3)′	110 (1)
O(5)–Hg(1)–C(1)	89 (2)	O(3)–Hg(2)–O(4)′	71 (1)
O(5)–Hg(1)–C(1)	92 (2)	O(4)–Hg(2)–O(4)′	108 (1)
O(1)–Hg(1)–O(5)	82 (1)	Ag(1)–N(1)–C(1)	173 (6)
Hg(2)–C(2)–N(2)	171 (5)	N(1)–Ag(1)–N(1)	162 (3)
Hg(2)–C(3)–N(3)	174 (6)	$H_2O(3)$–Ag(1)–N(1)	111 (2)
C(2)–Hg(2)–C(3)	176 (2)	$H_2O(3)$–Ag(1)–N(1)	81 (2)
O(2)–Hg(2)–C(2)	75 (2)	$H_2O(3)$–Ag(1)–$H_2O(3)$	98 (3)
O(2)–Hg(2)–C(3)	109 (2)	Ag(2)–N(2)–C(2)	178 (5)
O(3)–Hg(2)–C(2)	104 (2)	Ag(2)–N(3)–C(3)	166 (6)
O(3)–Hg(2)–C(3)	74 (2)	N(2)–Ag(2)–N(3)	163 (2)
O(3)′–Hg(2)–C(2)	91 (2)	$H_2O(2)$–Ag(2)–N(2)	101 (2)
O(3)′–Hg(2)–C(3)	86 (2)	$H_2O(2)$–Ag(2)–N(3)	90 (2)
O(4)–Hg(2)–C(2)	89 (2)	$H_2O(3)$–Ag(2)–N(2)	93 (2)
O(4)–Hg(2)–C(3)	93 (2)	$H_2O(3)$–Ag(2)–N(3)	101 (2)
O(4)′–Hg(2)–C(2)	82 (2)	$H_2O(2)$–Ag(2)–$H_2O(3)$	87 (2)
O(4)′–Hg(2)–C(3)	94 (2)	$H_2O(2)$–$H_2O(1)$–$H_2O(3)$	106 (2)

TABLE VIII

PARAMETERS FOR ELLIPSOIDS OF VIBRATION

Atom	Rms amplitude, Å	Angles with crystallographic axes, deg		
		a	b	c
Hg(1)	0.110 (7)	78 (3)	90	12 (3)
	0.131 (8)	90	180	90
	0.185 (5)	168 (3)	90	78 (3)
Hg(2)	0.108 (6)	48 (2)	121 (3)	59 (2)
	0.172 (4)	114 (8)	149 (3)	109 (10)
	0.186 (3)	128 (6)	91 (11)	38 (6)
Ag(1)	0.164 (10)	82 (5)	90	9 (5)
	0.242 (11)	90	180	90
	0.245 (9)	172 (5)	9	81 (5)
Ag(2)	0.135 (12)	40 (4)	68 (4)	60 (3)
	0.223 (8)	59 (6)	148 (8)	98 (9)
	0.253 (7)	113 (6)	111 (9)	32 (4)

Results and Discussion

The interatomic distances and angles pertaining to the coordination spheres about the mercury and silver atoms are listed in Tables VI and VII. The errors in these values were calculated without inclusion of correlation effects. In the group refinements the C–N distance was fixed at 1.156 Å.[11] The nitrate ion was treated as a planar group with all O–N–O angles 120° and all N–O distances 1.22 Å.[12] The *h*0*l* and *hk*0 projections are shown in Figure 1.

Table VIII lists parameters for the ellipsoids of vibration. The mercury and silver atoms are quite anisotropic, vibrating less in the direction of the chain than in other directions. The Hg(1) atom is also somewhat constrained along the *b* axis direction by the contacts that it makes with $NO_3(1)$.

The dominating structural feature in this compound is the two crystallographically independent sets of approximately linear chains, –Ag–NC–Hg–CN–Ag–. If the cyanide group occurs with its usual geometry and the Hg and Ag atoms are sp hybridized, we would expect the chains to be exactly linear. There are ten crystallographically independent angles that we would expect to be 180° for linear chains; these are listed in Table VII. Of these ten only three differ from 180° by more than two standard deviations; these are the two N–Ag–N angles and one of the Ag–N–C angles. A detailed ex-

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(11) D. Britton, *Perspect. Struct. Chem.*, **1,** 109 (1967).

(12) Reference 2, p 627.

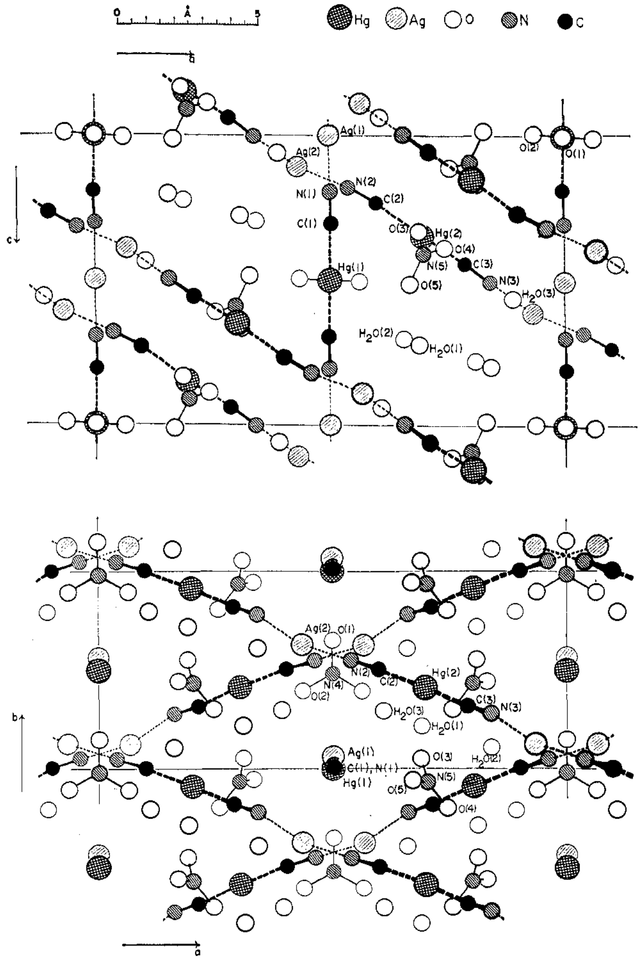

Figure 1.—The crystal structure of $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$.

amination of the environment of the Ag atoms, discussed below, makes these displacements at the Ag appear reasonable. The three independent Hg–C distances in the chain average 2.04 Å with an average deviation of 0.08 Å; the three independent Ag–N distances average 2.11 Å with an average deviation of 0.06 Å. A detailed examination of these distances might seem to suggest that one of the CN groups in the second chain is more closely associated with the mercury than the other; there is no apparent reason for this, however, and we are inclined to regard it as unreal. The average Hg–C distance compares well with the value of 2.015 (3) Å in $Hg(CN)_2$ determined by Seccombe and Kennard with neutron diffraction data.[13] The Ag–N average distance also appears reasonable although the available comparisons are less appropriate: the averages of the Ag–N distance and Ag–C distance in AgCN and in $AgCN \cdot 2AgNO_3$ are 2.05 and 2.06 Å, respectively; the Ag–N distance in AgNCO is 2.115 (8) Å, although the nitrogen has sp^2 hybridization in the isocyanate group rather than sp as in cyanide.[14]

The detailed environments of the two crystallographically independent Hg atoms are similar and do not differ from those commonly found for Hg(II). In the two polar directions there are the strong Hg–C bonds. In the equatorial direction there are a number of weaker Hg–O contacts. For Hg(1) the shortest of these Hg–O contacts is 2.55 Å, and there are two others at 2.85 Å and two at 3.06 Å. The Hg(2) atom also has five contacts with oxygen atoms, one each at 2.62, 2.82, 2.84, 2.92, and 2.95 Å, all more or less in the equatorial plane. The Hg environment in this compound may be compared, for example, to those in the orthorhombic and hexagonal forms of HgO, in both of which there are two short Hg–O distances, slightly over 2 Å, analogous to the Hg–C distances in our compound, and four more Hg–O distances between 2.79 and 2.90 Å.[15]

The detailed environments of the Ag atoms are both similar. Ag(1) forms two strong bonds to N atoms in cyanide groups with an angle of 162° between the bonds. There are also two Ag–O interactions with H_2O molecules 2.57 Å away. These are both on the opposite sides of the Ag from the two N atoms and, together with the N atoms, form a roughly tetrahedral arrangement. Ag(2) also forms two strong bonds to cyanide N atoms with an angle of 163° and also has two close oxygen neighbors, one at 2.56 Å and one at 2.55 Å. Again the latter are on the opposite side of the Ag from the two N atoms and complete a roughly tetrahedral arrangement. In both cases these two relatively short Ag–O contacts appear to be the cause of the distortion of the cyanide chain from linearity. In the case of the Ag(2) there is also perhaps another reason for this distortion: if the chain were perfectly linear, the Ag(2)–Ag(2) distance between the two chains related by a twofold axis would be close to 2.8 Å, shorter than the Ag–Ag distance in metallic silver, 2.89 Å. With the distortion in the chain this distance increases to 3.21 Å.

In summary, we would view this structure as composed of infinite chains of Ag atoms bridged with $Hg(CN)_2$ molecules. The chains are distorted slightly from linearity by relatively strong secondary interactions between the silver atoms and water molecules. The mercury atoms, as usually is the case, have a number of relatively weak secondary interactions, here with oxygen atoms in the nitrate and water molecules. It should be emphasized that we cannot decide from these data whether the CN groups are ordered or disordered, although we believe them to be ordered as shown in Figure 1 and as used in the Discussion.

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