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The Crystal Structure of Zinc Nitrate–2-Mercury(II) Cyanide–7-Water, $Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$

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Zinc nitrate–2-mercury(II) cyanide–7-water, $Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$, is monoclinic with $a = 17.598$ (13), $b = 6.639$ (2), $c = 16.112$ (9) Å, $\beta = 94.99$ (7)°; $Z = 4$, and space group C_{2h}^6-$C2/c$. The measured and calculated densities are 2.89 (1) and 2.907 (3) g/cm^3, respectively. The structure was determined with 954 intensities above background, collected by counter methods and refined by least squares to an R factor of 6.0%. Zn is octahedrally coordinated by four H_2O groups and two nearly linear $Hg(CN)_2$ groups. This compound should be formulated $[Zn(H_2O)_4(Hg(CN)_2)_2](NO_3)_2 \cdot 3H_2O$. Hydrogen bonds hold together the various groups in the structure. The bond lengths along Zn–N–C–Hg–C–N are 2.13 (2), 1.14 (4), 2.06 (3), 1.97 (3), and 1.18 (4) Å, respectively; bond angles are 173.5 (26), 175.9 (26), 174.1 (12), and 177.9 (28)°, respectively. Note is made of an unsuccessful attempt to solve the structure of $Cd(NO_3)_2 \cdot Hg(CN)_2 \cdot xH_2O$.

Introduction

A compound $Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$ was reported in 1859 by Nylander.[1,2] The structure of this compound was investigated as part of a study of cyanide bridging between metals of groups Ib and IIb.[3] It was thought originally that this structure might have a skeleton of zinc atoms on tetrahedral sites with four linear, bridging $Hg(CN)_2$ ligands, forming an infinite network.

Experimental Section

Prismatic crystals of the compound formed upon partial evaporation of an aqueous solution made up with 5 g of $Hg(CN)_2$ and 30 g of $Zn(NO_3)_2 \cdot xH_2O$ ($x = 3$–6). The large excess of the more soluble zinc nitrate was necessary to obtain the pure double salt rather than $Hg(CN)_2$ or a mixture. The mother liquor was filtered off and the product was washed with acetone. An infrared spectrum had weak cyanide bands at 2190 and 2230 cm^{-1}, as well as bands due to H_2O and NO_3^-.

Precession photographs were taken with Mo Kα radiation (λ 0.7107 Å). The crystal was mounted with the c axis along the spindle axis. The photographs indicated that the crystals are monoclinic, and the systematic extinctions, $h + k = 2n + 1$ for hkl reflections and $l = 2n + 1$ for $h0l$ reflections, indicated the space group C_s^4-Cc or C_{2h}^6-$C2/c$. The spoon test for pyroelectricity[4] was negative, therefore, inconclusive. The eventual solution fit the centric space group, $C2/c$.

Unit cell dimensions were determined by least-squares refinement using the θ angle values for 18 Mo Kα peaks scanned with a diffractometer. All of the data were collected at room temperature. The unit cell dimensions are $a = 17.598$ (13), $b = 6.639$ (2), $c = 16.112$ (9) Å, and $\beta = 94.99$ (7)°. The measured density is 2.89 (1) g/cm^3 from flotation in thallous formate–thallous malonate solution and is 2.87 (1) g/cm^3 from flotation in a CH_2I_2–CCl_4 mixture. This is in accord with the calculated density, 2.907 (3) g/cm^3, with $Z = 4$ formula units per cell.

The crystal used for collection of intensity data was ground to a sphere in a compressed-air abrasion chamber.[5] The crystal radius was about 0.084 mm. The crystal was glued onto a thin glass rod and sealed into a capillary containing a larger crystal to maintain the vapor pressure, preventing dehydration. Intensity data covering half the sphere of reflection were collected on a four-circle Hilger & Watts automatic diffractometer out to $\theta = 26°$. The takeoff angle was 3.0°. The crystal was 28 cm from the source and 20 cm from a 6.0-mm circular aperture. The incident beam was Zr-filtered Mo Kα radiation. Each peak was scanned at 0.3°/min in 90 2-sec steps of 0.01° in both θ and ω from -0.45 to $+0.45°$ from the calculated setting. The background was counted for 90 sec at each limit of the scan while crystal and counter were stationary.

The intensities of all reflections for which $l \geqslant 0$ were collected. After equivalents were combined, there were 1849 nonequivalent reflections, although only 954 had intensities above background, *i.e.*, with $|F|^2/\sigma_{|F|^2} \geqslant 2.4$. Two standard reflection intensities were checked at intervals of 50 sequential reflections. The data were collected intermittently over 1 month. The 20 different scale factors derived from a graph of standard intensities *vs.* time had a spread of 11.5%.

The raw data were scaled, equivalent reflections were combined, and average intensities (I) and their errors (σ_I) were calculated from the peak intensities (p) and combined right and left backgrounds (B) according to the equations[6]

$$I = \left(\sum_1^n p - \sum_1^n B\right)\Big/ n$$

$$\sigma_I = \sqrt{\sum_1^n p + \sum_1^n B + 0.002\left(\sum_1^n p - \sum_1^n B\right)^2 \Big/ n}$$

The absorption coefficient, μ, is 179.5 cm^{-1} for Mo Kα radiation. For the spherical crystal used in data collection, $\mu R = 1.50$. Values for the absorption factor were interpolated from Bond's table.[7] The usual Lorentz and polarization corrections were also made.

Structure Determination and Refinement

The zinc and mercury atoms were located with a three-dimensional Patterson map.[8] Following three

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(1) C. W. G. Nylander, *Oefvers. Akad. Stockholm*, **16**, 281 (1859); *J. Prakt. Chem.*, **79**, 379 (1860).

(2) In the same articles Nylander also reported preparing $Cd(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$ from a solution of $Cd(NO_3)$, in excess, and $Hg(CN)_2$. Repeated attempts were made to prepare this compound, but the only double salt found was $Cd(NO_3)_2 \cdot Hg(CN)_2 \cdot xH_2O$. Some of the efflorescent acicular crystals were mounted and sealed in capillary tubes. The cell dimensions of four different crystals, as measured from Weissenberg, oscillation, and precession photographs, varied considerably: $a = 28.3$ (1)–29.7 (1), $b = 25.9$ (1)–26.7 (1), $c = 6.64$ (2)–6.83 (2) Å. All belonged to space group C_{2v}^{19}–$Fdd2$ ($Z = 16$). Densities of the crystals from flotation varied, but most were 2.70–2.75 g/cm^3. It appears that the hydration number of this compound can vary within limits without a fundamental change in structure. An attempt was made to solve the structure with 1219 independent observed reflections. (Layers $hk0$–$hk7$ were collected by multiple-film Weissenberg technique using Mo Kα radiation and correlated with oscillation data.) Hg and Cd positions were located from a Patterson map and refined by least squares. Not all of the light atoms could be located from Fourier maps. The structure has a single Hg–Cd distance of about 5.41 Å, suggestive of Hg–CN–Cd. Efforts to find a cyanide group along the Hg–Cd line failed. The structure appears to have independent $Hg(CN)_2$ molecules and Cd atoms surrounded by a distorted array of oxygen atoms. No further work on this structure is planned.

(3) C. Mahon, Ph.D. Thesis, University of Minnesota, 1970; C. Mahon and D. Britton, *Inorg. Chem.*, **10**, 586 (1971).

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

(5) W. L. Bond, *Rev. Sci. Instrum.*, 344 (1951).

(6) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(7) W. L. Bond, "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1952, Table 5.3.6B, p 302.

(8) Three local programs were used to solve and refine the structure: UMPREL for statistics and Patterson map; UMLSTSG for full-matrix, least-squares refinement; and BADTEA for bond distances, angles, and errors. All data processing was done with the Control Data 6600 computer at the University of Minnesota Computer Center.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS)

H	L	FO	FC
**** K = 0 ****			
-20	4	128	131
-20	8	99	99
-18	2	198	194
-18	4	129	100
-18	6	97	89
-18	8	101	123
-18	12	118	116
-16	4	194	190
-16	6	235	239
-16	8	132	117
-16	10	105	112
-16	12	97	117
-14	2	162	165
-14	4	212	212
-14	6	98	59
-14	8	240	244
-14	10	217	212
-14	14	103	114
-14	16	89	86
-12	2	376	374
-12	6	161	163
-12	8	220	210
-12	12	201	197
-12	14	160	171
-10	4	399	408
-10	6	341	331
-10	10	215	208
-10	12	141	150
-10	16	188	194
-10	18	85	125
-8	2	422	427
-8	4	189	175
-8	8	456	449
-8	10	278	274
-8	14	176	180
-8	18	100	74
-6	2	392	415
-6	4	81	77
-6	6	386	360
-6	8	77	79
-6	10	210	196
-6	12	319	311
-6	14	131	158
-6	18	87	113
-4	2	369	367
-4	4	377	369
-4	6	427	418
-4	10	214	216
-4	12	138	130
-4	14	139	140
-4	16	199	209
-4	18	111	101
-2	2	421	428
-2	4	210	195
-2	6	282	281
-2	8	484	482
-2	10	206	205
-2	12	163	145
-2	14	196	199
-2	18	121	119
0	2	318	335
0	4	246	206
0	6	517	537
0	10	179	177
0	12	340	327
0	18	104	107
2	2	362	402
2	4	674*	776
2	6	228	234
2	8	197	192
2	10	296	288
2	14	181	186
2	16	187	184
4	0	301	313
4	2	370	379
4	4	202	196
4	6	443	453
4	8	481	485
4	10	210	200
4	12	147	146
4	14	170	159
4	18	112	128
6	0	389	420
6	2	110	118
6	4	205	218
6	6	238	241
6	10	335	326
6	12	293	292
6	16	98	114
8	0	110	110
8	2	400	413
8	4	434	451
8	8	193	171
8	10	154	149
8	14	152	141
8	16	143	155
10	0	171	173
10	2	210	213
10	4	112	108
10	6	273	267
10	8	238	235
10	12	141	144
12	0	323	325
12	2	86	58
12	4	251	227
12	6	183	183
12	10	225	227
12	12	126	118
14	0	119	118
14	2	300	304
14	4	189	177
14	8	94	120
14	14	122	129
16	0	175	175
16	2	115	106
16	4	119	108
16	6	217	210
16	8	110	127
18	0	157	143
18	4	131	124
18	8	102	84
20	0	114	112
20	2	159	161
**** K = 1 ****			
-21	2	123	107
-21	4	104	69
-21	5	104	94
-19	3	121	107
-19	4	94	83
-19	6	109	133
-19	9	91	86
-17	1	154	150
-17	7	121	134
-17	10	129	143
-17	11	88	72
-15	2	185	199
-15	3	113	107
-15	4	81	76
-15	5	181	181
-15	6	97	87
-15	9	104	106
-15	11	130	119
-15	12	103	105
-15	14	112	114
-13	1	183	176
-13	3	193	206
-13	4	243	249
-13	6	197	202
-13	7	152	164
-13	9	164	169
-13	10	112	111
-13	12	101	80
-13	13	107	98
-13	15	97	91
-13	16	105	106
-11	1	206	205
-11	2	109	97
-11	4	131	119
-11	5	171	165
-11	7	179	167
-11	8	269	266
-11	10	158	163
-11	11	140	136
-11	13	117	124
-11	14	85	96
-9	2	272	275
-9	3	235	241
-9	5	255	249
-9	6	131	117
-9	9	224	219
-9	11	181	166
-9	12	206	205
-9	14	143	138
-9	15	128	134
-9	16	110	12
-9	17	99	86
-7	1	297	308
-7	2	121	134
-7	3	295	294
-7	4	324	328
-7	5	82	44
-7	6	278	270
-7	7	234	222
-7	9	167	159
-7	10	113	113
-7	12	101	57
-7	13	165	148
-7	15	113	76
-7	16	145	151
-7	18	96	77
-5	1	208	218
-5	2	408	411
-5	3	212	209
-5	4	148	138
-5	5	338	330
-5	6	202	191
-5	7	223	206
-5	8	409	396
-5	10	171	167
-5	11	193	191
-5	13	110	129
-5	14	106	111
-5	17	112	105
-5	18	78	74
-3	1	183	161
-3	2	301	270
-3	3	404	397
-3	4	172	170
-3	5	238	230
-3	6	283	274
-3	7	127	120
-3	9	260	257
-3	10	134	147
-3	11	148	136
-3	12	270	268
-3	13	98	81
-3	15	139	144
-1	1	412	414
-1	2	332	336
-1	3	223	185
-1	4	408	434
-1	5	306	303
-1	6	245	238
-1	7	414	415
-1	9	129	128
-1	10	158	157
-1	11	174	168
-1	13	220	209
-1	14	109	109
-1	16	161	164
-1	19	106	86
1	0	145	155
1	1	178	189
1	2	172	171
1	3	238	211
1	4	83	86
1	5	267	279
1	6	239	240
1	7	76	66
1	8	292	288
1	9	185	184
1	10	176	176
1	11	213	200
1	12	98	52
1	14	101	109
1	15	111	97
1	17	116	105
3	0	501	518
3	1	275	239
3	2	200	187
3	3	286	308
3	4	153	163
3	5	81	79
3	6	293	294
3	7	197	193
3	9	248	228
3	10	238	245
3	12	221	205
3	13	155	143
3	15	145	145
5	0	192	189
5	1	402	420
5	2	304	326
5	3	224	215
5	4	360	372
5	5	195	197
5	6	85	67
5	7	235	242
5	10	133	137
5	11	154	153
5	12	88	26
5	13	116	117
5	14	135	144
5	16	118	120
5	17	103	96
7	0	151	158
7	2	206	209
7	3	318	311
7	4	74	73
7	5	284	281
7	6	292	290
7	8	282	277
7	9	203	195
7	11	144	147
7	12	91	103
7	14	90	72
7	15	99	96
9	0	349	360
9	1	237	243
9	2	137	132
9	3	222	213
9	4	193	176
9	6	131	118
9	7	158	160
9	9	166	153
9	10	167	167
9	12	153	139
9	13	100	97
9	16	90	64
11	0	68	82
11	1	168	174
11	2	225	220
11	4	233	230
11	5	201	205
11	7	172	153
11	8	120	126
11	11	134	133
11	13	112	96
11	14	96	107
13	0	114	107
13	2	84	95
13	3	191	191
13	4	104	78
13	5	118	121
13	6	165	162
13	8	116	121
13	9	146	133
15	0	167	168
15	1	188	177
15	4	85	88
15	7	129	139
15	9	95	56
15	10	102	126
17	2	157	168
17	4	130	123
17	5	93	112
19	3	114	108
19	6	115	100
21	0	76	60
**** K = 2 ****			
-20	1	152	135
-20	7	111	129
-18	5	161	162
-18	11	126	128
-16	1	123	129
-16	3	188	194
-16	7	117	124
-16	9	145	153
-16	13	90	94
-14	1	200	198
-14	4	87	59
-14	5	157	157
-14	7	192	186
-14	11	148	143
-14	13	130	139
-12	3	241	247
-12	5	259	267
-12	7	90	15
-12	9	185	179
-12	10	83	74
-12	11	171	174
-12	15	133	124
-10	1	316	322
-10	3	312	319
-10	4	81	75
-10	7	280	285
-10	9	203	201
-10	13	157	165
-10	15	112	112
-8	1	351	358
-8	2	95	112
-8	4	141	158
-8	5	354	359
-8	7	308	293
-8	11	231	227
-8	13	143	158
-8	17	90	116
-6	1	80	92
-6	2	150	134
-6	3	383	377
-6	4	162	145
-6	5	301	304
-6	7	110	92
-6	8	118	112
-6	9	358	345
-6	11	217	211
-6	15	204	208
-4	1	543	533
-4	2	107	123
-4	3	394	365
-4	5	204	200
-4	7	400	406
-4	8	102	106
-4	9	224	223
-4	10	88	64
-4	11	130	120
-4	12	109	93
-4	13	241	234
-4	15	102	106
-4	19	104	110
-2	1	270	261
-2	2	149	144
-2	3	288	271
-2	4	125	129
-2	5	383	398
-2	6	107	103
-2	7	162	151
-2	9	230	215
-2	11	267	268
-2	13	102	110
-2	15	100	113
-2	17	133	153
0	0	90	106
0	1	224	225
0	3	414	434
0	5	268	270
0	6	165	170
0	7	202	199
0	8	114	107
0	9	336	339
0	11	140	136
0	13	154	155
0	15	165	180
0	16	88	20
2	1	403	420
2	3	173	168
2	4	116	126
2	5	284	278
2	6	110	81
2	7	333	341
2	9	89	91
2	11	216	221
2	12	92	78
2	13	224	222
2	17	113	130
4	0	195	196
4	1	153	157
4	2	78	76
4	3	374	381
4	4	96	102
4	5	370	382
4	9	220	218
4	11	194	217
4	12	108	82
4	15	90	115
4	17	110	111
6	1	283	293
6	2	71	70
6	3	337	345
6	4	172	167
6	6	119	101
6	7	263	255
6	9	233	224
6	13	165	157
6	15	113	131
8	1	371	378
8	2	85	90
8	5	281	284
8	7	282	291
8	10	114	89
8	11	176	193
8	13	136	142
10	0	74	86
10	3	321	315
10	4	92	70
10	5	239	225
10	9	209	216
10	11	146	134
10	15	110	120
12	1	320	314
12	3	217	230
12	4	115	91
12	5	90	43
12	7	222	220
12	9	149	142
12	13	131	118
14	1	166	167
14	5	194	197
14	7	142	133
14	11	140	136
16	3	181	186
16	5	107	113
16	9	145	138
16	11	90	70
18	1	131	152
18	7	119	112
**** K = 3 ****			
-19	2	113	105
-19	7	95	65
-17	1	104	107
-17	2	125	109
-17	4	199	180
-17	5	92	95
-17	11	97	75
-15	2	127	115
-15	5	116	114
-15	6	119	117
-15	8	160	161
-15	9	98	104
-15	11	88	82
-13	1	114	125
-13	3	139	143
-13	4	109	109
-13	6	121	144
-13	7	87	109
-13	9	113	102
-13	10	153	163
-13	12	173	164
-13	13	110	94
-11	1	172	178
-11	2	274	274
-11	4	234	239
-11	5	131	133
-11	7	115	129
-11	8	117	117
-11	10	105	103
-11	13	94	75
-11	14	147	139
-11	16	125	107
-9	2	184	167
-9	3	199	198
-9	4	112	91
-9	5	182	186
-9	6	283	290
-9	8	237	234
-9	9	145	143
-9	11	120	102
-9	12	100	102
-7	1	213	202
-7	3	130	139
-7	4	135	136
-7	5	90	80
-7	6	181	128
-7	7	192	193
-7	9	123	136
-7	10	242	224
-7	12	157	165
-7	13	108	112
-7	16	91	92
-5	1	137	131
-5	2	396	382
-5	3	149	145
-5	4	313	295
-5	5	231	215
-5	7	124	108
-5	8	249	238
-5	9	103	97
-5	11	159	170
-5	14	210	219
-5	16	86	81
-5	17	94	79
-3	1	113	106
-3	2	174	156
-3	3	282	263
-3	4	221	209
-3	5	96	115
-3	6	348	352
-3	7	144	143
-3	8	158	162
-3	9	185	172
-3	11	99	63
-3	12	99	108
-3	13	113	85
-3	15	106	116
-3	16	117	74
-3	18	122	121
-1	1	269	262
-1	2	175	152
-1	3	202	194
-1	4	192	183
-1	5	146	143
-1	6	120	127
-1	7	219	228
-1	8	219	225
-1	10	255	256
-1	11	138	130
-1	12	187	178
-1	13	107	128
-1	16	101	78
1	0	231	225
1	1	140	133
1	2	419	413
1	3	168	153
1	4	303	306
1	5	241	222
1	6	114	111
1	7	105	114
1	8	184	184
1	9	122	124
1	11	164	146
1	12	173	180
1	14	163	155
3	0	344	330
3	1	243	236
3	3	239	240
3	4	287	291
3	6	389	390
3	7	149	145
3	9	168	164
3	12	176	174
3	15	107	96
3	16	113	111
3	18	138	102
5	0	146	136
5	1	254	249
5	2	144	119
5	3	82	85
5	4	219	222
5	5	193	191
5	7	187	183
5	8	191	203
5	10	223	218
5	11	108	111
7	0	347	351
7	1	84	92
7	2	251	259
7	3	131	148
7	4	80	79
7	5	188	184
7	6	175	175
7	8	114	109
7	9	148	144
7	11	94	115
7	12	187	177
7	14	140	144
9	0	144	150
9	1	157	147
9	3	162	152
9	4	276	269
9	6	226	217
9	7	111	109
9	9	125	115
9	10	145	141
9	13	100	87
11	1	172	155
11	2	185	172
11	4	112	110
11	5	158	135
11	6	133	130
11	7	99	100
11	8	177	182
11	10	144	124
11	11	88	80
13	0	213	207
13	2	179	187
13	3	145	149
13	5	95	106
13	6	99	87
13	10	87	71
13	12	104	107
15	0	81	60
15	1	110	122
15	2	96	70
15	4	189	190
15	6	110	106
17	2	90	101
17	8	119	111
19	0	120	127
19	2	102	60
19	3	111	79
**** K = 4 ****			
-18	2	129	120
-18	6	115	107
-16	2	117	94
-16	4	101	104
-16	6	141	143
-16	10	112	119
-14	2	201	206
-14	4	218	221
-14	8	125	133
-14	10	103	129
-12	2	169	171
-12	6	232	239
-12	8	210	210
-12	12	106	112
-12	14	90	95
-10	4	151	141
-10	6	119	134
-10	10	250	243
-10	12	165	173
-8	2	323	329
-8	4	295	284
-8	7	98	37
-8	8	172	181
-8	10	109	94
-8	12	103	90
-8	14	184	189
-8	16	108	102
-6	2	149	138
-6	4	145	151
-6	6	304	301
-6	8	222	200
-6	12	117	140
-6	16	111	97
-4	3	85	70
-4	4	298	266
-4	6	176	162
-4	7	93	85
-4	8	155	149
-4	10	236	260
-4	12	155	152
-2	2	463	458
-2	4	245	232
-2	5	89	27
-2	6	116	84
-2	8	247	251
-2	12	128	138
-2	14	214	212
0	0	344	328
0	2	115	115
0	3	88	63
0	4	250	250
0	6	432	441
0	8	168	165
0	12	179	181
2	0	231	230
2	2	193	177
2	4	247	241
2	8	242	248
2	10	241	260
2	12	117	96
2	14	99	85
2	16	121	111
4	0	329	316
4	2	394	401
4	4	206	199
4	5	110	74
4	6	156	156
4	8	200	208
4	12	193	201
4	14	159	167
6	0	298	291
6	4	302	299
6	6	317	323
6	10	117	131
6	12	106	117
8	1	85	69
8	2	178	178
8	4	208	211
8	5	101	47
8	8	200	208
8	10	218	220
10	0	246	243
10	2	229	230
10	6	162	156
10	8	115	111
10	12	167	147
12	0	135	131
12	4	241	226
12	6	161	155
12	10	108	112
14	2	130	133
14	4	106	90
14	8	160	157
16	0	213	206
16	2	159	147
16	6	102	98
18	2	92	71
**** K = 5 ****			
-17	1	90	102
-17	2	111	90
-15	3	92	71
-15	5	109	122
-15	6	100	106
-15	8	107	83
-13	1	119	116
-13	3	155	157
-13	4	86	68
-13	7	121	103
-13	9	109	115
-13	10	106	108
-11	1	157	164
-11	2	173	176
-11	4	89	120
-11	5	123	127
-11	7	142	143
-11	11	85	93
-11	12	86	63
-9	3	182	194
-9	5	193	180
-9	6	190	190
-9	9	156	160
-9	11	114	138
-7	1	206	211
-7	3	191	187
-7	4	113	126
-7	7	181	191
-7	8	86	89
-7	9	121	128
-7	10	150	163
-7	13	114	119
-5	1	132	143
-5	2	185	172
-5	4	173	153
-5	5	224	221
-5	7	149	133
-5	11	159	158
-5	12	95	89
-5	13	96	103
-5	14	125	116
-3	3	204	201
-3	4	143	129
-3	5	184	131
-3	6	182	176
-3	8	100	113
-3	9	166	188
-3	11	97	92
-3	15	120	117
-1	1	304	305
-1	3	122	119
-1	4	101	113
-1	5	144	133
-1	7	219	223
-1	8	99	102
-1	10	160	152
-1	11	126	102
-1	13	135	151
1	0	122	125
1	1	140	127
1	2	284	284
1	3	157	153
1	4	134	104
1	5	245	243
1	8	98	102
1	9	92	100
1	11	153	133
3	0	103	102
3	1	145	142
3	3	252	246
3	4	148	146
3	5	90	74
3	6	194	193
3	7	136	149
3	9	176	192
3	15	113	97
5	0	138	114
5	1	207	212
5	2	100	71
5	4	111	92
5	5	142	134
5	7	169	181
5	8	144	149
5	10	132	138
5	11	109	118
5	13	103	109
7	0	169	168
7	2	189	183
7	3	173	186
7	5	171	161
7	9	119	133
7	11	113	112
9	0	86	99
9	1	161	173
9	3	156	165
9	4	136	124
9	6	135	150
9	7	130	123
11	1	167	139
11	5	139	145
11	7	114	119
11	10	101	85
11	11	93	105
13	0	123	125
13	2	137	123
13	3	120	149
13	9	122	101
15	0	77	57
15	1	135	138
15	4	95	101
**** K = 6 ****			
-14	1	119	130
-14	5	116	115
-12	2	74	82
-12	3	137	134
-12	5	142	142
-10	1	168	170
-10	3	160	150
-10	6	98	76
-10	7	137	146
-10	9	118	113
-8	1	180	174
-8	5	181	187
-8	7	148	138
-6	11	125	132
-6	2	109	104
-6	3	238	238
-6	9	165	180
-4	1	248	244
-4	2	97	91
-4	3	169	162
-4	6	131	115
-4	7	229	224
-4	9	128	114
-4	13	131	140
-2	1	106	119
-2	3	94	105
-2	5	225	225
-2	7	92	108
-2	9	102	94
-2	11	175	172
0	0	131	146
0	1	116	119
0	3	221	219
0	5	84	82
0	9	171	179
0	12	104	68
2	1	210	216
2	3	84	79
2	4	85	66
2	5	107	134
2	7	178	177
2	11	119	116
2	13	93	120
4	3	136	150
4	5	194	196
4	9	122	120
4	11	122	119
6	0	67	69
6	1	166	172
6	3	185	197
6	7	121	127
6	9	140	136
8	1	206	212
8	2	86	93
8	5	162	158
8	7	136	150
10	3	133	162
10	5	139	147
10	9	124	116
12	1	137	145
12	3	94	126
14	1	100	101
**** K = 7 ****			
-11	2	86	79
-9	2	158	160
-9	3	99	75
-7	4	137	144
-7	6	140	152
-5	2	129	133
-5	5	94	92
-5	8	159	163
-3	2	158	149
-3	3	122	104
-3	6	135	118
-1	1	105	98
-1	2	135	117
-1	4	190	196
-1	6	106	124
-1	10	99	92
1	2	92	120
1	4	92	61
1	6	106	109
1	8	160	158
1	10	99	88
3	0	204	212
3	3	107	98
3	6	117	125
5	1	102	94
5	2	173	162
5	4	173	169
7	0	98	92
7	2	108	88
7	5	90	75
7	6	138	149
9	0	147	146
11	1	111	67
**** K = 8 ****			
-2	2	108	125
0	0	203	193
0	2	96	111
2	2	128	123
4	0	78	75

* INDICATES REFLECTION WAS AFFECTED BY EXTINCTION, HENCE WAS GIVEN ZERO WEIGHT ON LAST CYCLE OF LEAST SQUARES REFINEMENT.

cycles of isotropic least-squares refinement upon the heavy-atom parameters, a Fourier map was calculated. All of the nonhydrogen atoms were found on this map. At this point the agreement factors were $R = 0.189$ and $r = 0.161$.[9]

Initially, all reflections with $|F|^2/\sigma_{|F|^2} \geqslant 1.0$ were used. After the first three cycles of refinement, a plot of $|F_o|$ *vs.* $|F_c|$ revealed that only data for which $|F|^2/\sigma_{|F|^2} \geqslant 2.4$ should be considered observed. Only these were used henceforth.

With thermally isotropic light atoms and anisotropic heavy atoms included, the agreement factors dropped immediately to $R = 0.118$ and $r = 0.060$. After five cycles of least-squares refinement, $R = 0.0622$ and $r = 0.0132$. In order to check the assumption that the carbon atom of each cyanide group is bonded to Hg, C(1) was interchanged with N(1), and C(2), with N(2). Starting with the parameters at the end of the last cycle, one cycle of least-squares refinement was calculated. The agreement factors increased to $R = 0.0634$ and $r = 0.0138$, and the temperature factors for the series of atoms Zn–X–X′–Hg–X′–X changed from 2.1, 2.7, 2.4, 2.5, 3.8, and 5.4 Å², respectively, for X = N and X′ = C to 2.1, 0.9, 3.9, 2.5, 5.3, and 2.9 Å², respectively, for X = C and X′ = N. This evidence strongly supports the contention that carbon, not nitrogen, bonds to mercury.

Then, with carbon and nitrogen atoms back in the original order, three more cycles of least-squares refinement with all atoms thermally anisotropic were calculated. The final values were $R = 0.0602$ and $r = 0.0118$. Hamilton's significance test[10] showed the anisotropic model to be preferred at the 99% confidence level.

The standard deviation of an observation of unit weight was 1.23. A graph of $|F_o|$ *vs.* $|F_c|$ showed that only the most intense reflection may be affected by extinction; hence, it was given zero weight on the last cycle of refinement. A final difference map showed

TABLE II

FINAL POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS[a]

Atom	Position	x	y	z	B,[b] Å²
Hg	8(f)	0.34182 (7)	0.86891 (18)	0.08530 (7)	2.53 (2)
Zn	4(a)	1/2	1/2	0	2.05 (11)
H_2O(1)	4(e)	1/2	0.4231 (41)	1/4	3.9 (9)
H_2O(2)	8(f)	0.4049 (9)	0.6536 (29)	−0.0597 (10)	2.7 (5)
H_2O(3)	8(f)	0.4875 (11)	0.6605 (27)	0.1111 (10)	3.1 (5)
H_2O(4)	8(f)	0.2091 (11)	0.0611 (30)	0.1421 (12)	3.9 (6)
O(1)	8(f)	0.4370 (11)	0.0079 (31)	0.3530 (12)	3.8 (6)
O(2)	8(f)	0.3738 (13)	0.1648 (34)	0.2508 (14)	5.1 (6)
O(3)	8(f)	0.3854 (14)	0.8319 (30)	0.2502 (12)	4.7 (7)
N(3)	8(f)	0.3999 (14)	0.0044 (38)	0.2848 (17)	3.2 (5)
N(1)	8(f)	0.4283 (14)	0.2649 (33)	0.0378 (14)	3.0 (7)
C(1)	8(f)	0.3964 (14)	0.1302 (48)	0.0564 (15)	2.4 (7)
N(2)	8(f)	0.2498 (16)	0.4693 (47)	0.1091 (20)	5.2 (7)
C(2)	8(f)	0.2837 (16)	0.6198 (50)	0.1016 (21)	3.8 (7)

[a] Estimated standard deviations (in parentheses) occur in the last digit. [b] B is the isotropic equivalent to the anisotropic temperature factor after the final cycle of refinement.

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(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; the weights were proportional to $(LpA\sigma_I)^{-2}$, where Lp and A were the Lorentz-polarization and absorption factors, respectively.

(10) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1956).

TABLE III

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	22.1 (3)	114.0 (21)	28.0 (4)	−13.6 (14)	4.1 (3)	4.3 (16)
Zn	18.2 (15)	98.4 (104)	21.7 (19)	0.1 (33)	4.5 (14)	5.3 (37)
$H_2O(1)$	46 (13)	182 (91)	28 (13)	0	10 (11)	0
$H_2O(2)$	22 (6)	189 (55)	21 (7)	4 (18)	1 (5)	3 (20)
$H_2O(3)$	39 (8)	131 (53)	23 (7)	10 (18)	13 (6)	−2 (18)
$H_2O(4)$	31 (8)	227 (64)	36 (11)	−13 (18)	−4 (8)	−27 (21)
{O(1)	33 (8)	222 (61)	30 (10)	28 (20)	−18 (8)	−16 (21)
O(2)	52 (11)	206 (79)	48 (12)	28 (23)	−5 (9)	23 (24)
O(3)	76 (13)	156 (70)	18 (9)	−29 (23)	−3 (8)	−8 (19)
N(3)	27 (10)	162 (71)	36 (14)	14 (24)	18 (10)	−34 (27)
{N(1)	40 (11)	82 (59)	27 (12)	−14 (22)	14 (9)	−7 (23)
C(1)	29 (10)	103 (60)	21 (11)	33 (19)	7 (13)	33 (36)
{N(2)	30 (11)	292 (95)	65 (19)	33 (29)	3 (13)	−14 (36)
C(2)	28 (11)	87 (65)	63 (18)	−25 (33)	7 (12)	14 (42)

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

one peak of height 1.8 $e^-/Å^3$ close to the Hg and O(3) positions and no others higher than 1.2 $e^-/Å^3$.

The final observed and calculated structure factors with absolute scaling are listed in Table I. The final atomic coordinates and thermal parameters are listed in Tables II and III. The scattering factors and heavy-atom anomalous scattering coefficients were taken from ref 11.

Nothing about the anisotropic thermal parameters or the agreement factors suggested that the space group might be the acentric *Cc* rather than *C*2/*c*.

Results and Discussion

The interatomic distances and angles are given in Tables IV and V. Each table is divided into a list for atoms interacting directly and a list for atoms presumably linked by hydrogen bonds. The errors given were calculated with correlation effects included. The structure is shown in Figure 1.

TABLE IV

PRINCIPAL INTERATOMIC DISTANCES

Direct interaction		Possible H-bonded interaction	
Distance	Value, Å	Distance	Value, Å
Hg–C(1)	2.06 (3)	O(2)--H-OH(1)	2.81 (3)
Hg–C(2)	1.97 (3)		
Hg–O(3)	2.71 (2)	O(1)--H-OH(2)	2.74 (3)
Hg–$H_2O(2)$	3.03 (2)	$H_2O(4)$--H-OH(2)	2.71 (3)
Hg–$H_2O(3)$	2.91 (2)		
Hg–$H_2O(4)$	2.88 (2)	$H_2O(1)$--H-OH(3)	2.73 (2)
		O(1)--H-OH(3)	2.70 (3)
Zn–N(1)	2.13 (2)		
Zn–$H_2O(2)$	2.12 (2)	N(2)--H-OH(4)	2.86 (4)
Zn–$H_2O(3)$	2.11 (2)		
		O(3)--H-OH(4)	3.08 (3)
N(3)–O(1)	1.23 (3)		
N(3)–O(2)	1.26 (3)		
N(3)–O(3)	1.29 (3)		
C(1)–N(1)	1.11 (4)		
C(2)–N(2)	1.18 (4)		

Table VI lists parameters for ellipsoids of vibration. The ellipsoids show that the mercury atom and cyanide groups are more constrained in the bonding direction, but the zinc atom is nearly isotropic.

The structure contains the tetraaquobis(dicyanomercury(II))zinc(II) cation and should be formulated as $[Zn(H_2O)_4(Hg(CN)_2)_2](NO_3)_2 \cdot 3H_2O$. The zinc atom, located on a center of symmetry, has sp^3d^2 orbital hybridization and a nearly regular octahedral

TABLE V

PRINCIPAL INTERATOMIC ANGLES

Direct interaction		Possible H-bonded interaction	
Angle	Value, deg	Angle	Value, deg
Hg–C(2)–N(2)	177.9 (28)	HO–H(3)–$H_2O(1)$–H–OH(3)	109.5 (12)
C(1)–Hg–C(2)	174.1 (12)	O(2)–$H_2O(1)$–H-OH(3)	110.4 (6)
Hg–C(1)–N(1)	175.9 (26)	O(2)–$H_2O(1)$–H–OH(3)	110.9 (6)
Zn–N(1)–C(1)	173.5 (26)	O(2)–H–O–H(1)–O(2)	104.7 (13)
N(1)–Zn–$H_2O(2)$	88.9 (8)	O(1)–H–O–H(2)–$H_2O(4)$	110.9 (8)
N(1)–Zn–$H_2O(3)$	88.9 (8)	O(1)–H–O–H(3)–$H_2O(1)$	108.3 (8)
$H_2O(2)$–Zn–$H_2O(3)$	89.7 (7)	O(3)–H–O–H(4)–N(2)	73.1 (8)
O(1)–N(3)–O(2)	121.0 (26)		
O(1)–N(3)–O(3)	118.2 (23)		
O(2)–N(3)–O(3)	120.7 (23)		

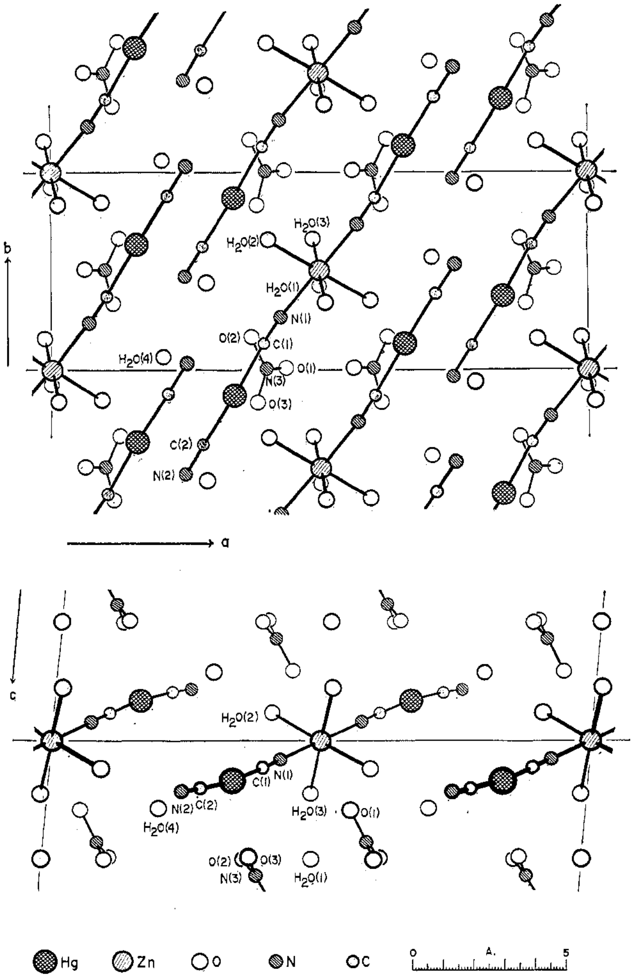

Figure 1.—The crystal structure of $Zn(NO_3)_2 \cdot 2Hg(CN)_2 \cdot 7H_2O$: top, view along *c* sin *β*, half unit cell in depth from −2.3 to +5.7 Å; bottom, view along *b*.

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(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A, p 202; Table 3.3.2C, p 215.

TABLE VI

PARAMETERS FOR ELLIPSOIDS OF VIBRATION

Atom	Rms amplitude, Å	—Angles with crystallographic axes, deg— *a*	*b*	*c*
Hg	0.140 (3)	59 (2)	34 (2)	104 (2)
	0.192 (2)	106 (10)	68 (5)	25 (9)
	0.199 (2)	36 (5)	114 (5)	70 (11)
Zn	0.143 (9)	75 (19)	31 (22)	118 (16)
	0.159 (9)	137 (16)	61 (23)	57 (17)
	0.180 (7)	51 (13)	79 (11)	46 (12)
$H_2O(1)$	0.18 (5)	107 (22)	90	12 (22)
	0.20 (5)	90	180	90
	0.27 (4)	17 (22)	90	78 (22)
$H_2O(2)$	0.16 (3)	86 (53)	97 (41)	11 (56)
	0.19 (3)	165 (68)	77 (67)	80 (56)
	0.21 (3)	104 (68)	165 (62)	94 (39)
$H_2O(3)$	0.15 (4)	65 (13)	116 (57)	146 (48)
	0.17 (4)	86 (26)	28 (56)	118 (55)
	0.26 (2)	25 (12)	82 (16)	71 (12)
$H_2O(4)$	0.17 (4)	63 (21)	55 (17)	50 (19)
	0.24 (3)	29 (37)	115 (74)	108 (68)
	0.25 (3)	99 (83)	135 (55)	45 (41)
O(1)	0.13 (5)	51 (11)	97 (20)	44 (14)
	0.20 (4)	74 (18)	153 (14)	113 (19)
	0.30 (3)	137 (10)	116 (14)	55 (8)
O(2)	0.18 (5)	69 (13)	144 (20)	64 (19)
	0.26 (3)	99 (30)	123 (23)	144 (28)
	0.30 (3)	157 (17)	103 (21)	66 (29)
O(3)	0.14 (4)	83 (10)	64 (40)	29 (40)
	0.19 (4)	82 (11)	28 (37)	118 (41)
	0.35 (3)	169 (9)	79 (9)	82 (7)
N(3)	0.09 (10)	125 (18)	55 (19)	51 (13)
	0.22 (4)	49 (32)	41 (29)	98 (30)
	0.26 (3)	61 (30)	109 (32)	40 (15)
N(1)	0.13 (5)	80 (38)	10 (26)	89 (70)
	0.16 (5)	64 (23)	93 (75)	158 (17)
	0.27 (3)	28 (17)	100 (12)	68 (17)
C(1)	0.07 (14)	75 (34)	143 (20)	58 (37)
	0.16 (6)	49 (30)	106 (32)	139 (43)
	0.25 (3)	44 (19)	58 (13)	68 (20)
N(2)	0.18 (5)	34 (21)	123 (20)	97 (21)
	0.27 (5)	62 (33)	48 (44)	59 (64)
	0.30 (4)	107 (35)	119 (51)	32 (63)
C(2)	0.10 (9)	64 (23)	27 (22)	99 (17)
	0.22 (5)	154 (23)	64 (23)	87 (31)
	0.29 (4)	88 (27)	84 (23)	9 (17)

environment. Zinc favors octahedral coordination with the less polarizable ligands, such as H_2O.[12] As mentioned in footnote 2, cadmium nitrate does not form a double salt isomorphous with $[Zn(H_2O)_4(Hg(CN)_2)_2](NO_3)_2 \cdot 3H_2O$. Cadmium seems to favor a distorted tetrahedral coordination with water ligands.[13] It has only slightly less affinity for cyanide ligands than zinc,[14] but the difference may be greater in affinity for the nitrogen end of the cyanide group.

In $[Zn(H_2O)_4(Hg(CN)_2)_2](NO_3)_2 \cdot 3H_2O$ the Zn–N distance, 2.13 (2) Å, is comparable to 2.10 (1) Å in $Zn(C_6H_4O_2N)_2 \cdot 4H_2O$[15] and in $Zn(C_9H_6ON)_2 \cdot 2H_2O$,[16] although in these two cases, N is sp^2, not sp, hybridized. The $Zn–OH_2$ distances, 2.12 (2) and 2.11 (2) Å, can be compared with the reported values (most given without error estimates): 2.03 Å in $Zn(NO_3)_2 \cdot 2H_2O$;[17] 2.05, 2.08, and 2.14 Å in $Zn(CH_3C_6H_4SO_3)_2 \cdot 6H_2O$;[18] 2.12 Å in $Zn(BrO_3)_2 \cdot 6H_2O$,[19] 2.14 Å in $Zn(CH_3COO)_2 \cdot 2H_2O$;[20] 2.18 (1) Å in $Zn(C_6H_4O_2N)_2 \cdot 4H_2O$;[15] and 2.26 Å in $Zn(C_9H_6ON)_2 \cdot 2H_2O$.[16]

The Hg–C distances, 2.06 (3) and 1.97 (3) Å, may be compared with 2.015 (3) Å in $Hg(CN)_2$ from a neutron diffraction study,[21] 1.97 (4) and 2.02 (4) Å in $(HgCN)_2O$,[22] and distances averaging 2.04 (8) Å in $Hg(CN)_2 \cdot AgNO_3 \cdot 2H_2O$.[3] The $Hg(CN)_2$ ligands are nearly linear, but the C–Hg–C angle, 174.1 (12°), is slightly bent, apparently due to the weak Hg–O(3) interaction.

A bridging cyanide group is known to have a slightly higher vibrational stretching frequency than a nonbridging cyanide.[23] This fact has been used to conclude from the infrared spectra that $Hg(CN)_2$ serves as a bridging and a nonbridging ligand in some double salts of $Hg(CN)_2$ with tetrahalides of tin and titanium.[24] The infrared spectrum of $[Zn(H_2O)_4(Hg(CN)_2)_2](NO_3)_2 \cdot 3H_2O$ has cyanide bands at 2190 and 2230 cm^{-1}, which can be assigned to the nonbridging and bridging cyanide groups, respectively.

The mercury atom would be expected to bond to the carbon end of the cyanide group. Better agreement factors and more reasonable temperature factors were obtained when the cyanide carbon atoms were placed adjacent to the mercury atom than when the ordering was reversed. The bond distances 1.11 Å for C(1)–N(1) and 1.18 (4) Å for C(2)–N(2) are within the limits of error of the typical distance 1.15–1.16 Å for C–N.[25]

The nitrate group is regular within the limits of error. The N–O bond lengths average 1.26 (3) Å, and the angles are all 120° within limits of error. Normal N–O bond lengths in NO_3^- range from 1.21 to 1.27 Å.[17]

All groups in the structure are linked by a network of hydrogen bonds. The bond angles and distances for possible hydrogen-bonded interaction listed in Tables IV and V show that probably all hydrogen atoms, except for one on $H_2O(4)$, participate. The hydrogen-bonding distances 2.70 (3)–2.86 (4) Å are typical,[26] and the angles about $H_2O(1)$, $H_2O(2)$, and $H_2O(3)$ are close to an H–O–H bond angle. The O(3)–$H_2O(4)$ distance, 3.08 (3) Å, could represent a weak hydrogen-bonded interaction, but the angle 73.1 (8)° about $H_2O(4)$ makes it unlikely to be a hydrogen bond.

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(12) R. S. Nyholm, *Proc. Chem. Soc., London*, 281 (1961).

(13) B. Matkovic and B. Ribar, *Croat. Chem. Acta*, **35**, 147 (1963).

(14) B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966).

(15) P. Lumme, G. Lundgren, and W. Mark, *Acta Chem. Scand.*, **23**, 3011 (1969).

(16) G. Palenik, *Acta Crystallogr.*, **17**, 696 (1964).

(17) B. Ribar, W. Nowacki, M. Sljukic, S. Scavnicar, and F. Gabela, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **129**, 305 (1969).

(18) A. Hargreaves, *Acta Crystallogr.*, **10**, 191 (1957).

(19) S. H. Yü and C. A. Beevers, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **95**, 426 (1936).

(20) J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Crystallogr.*, **6**, 720 (1953).

(21) R. C. Seccombe and C. H. L. Kennard, *J. Organometal. Chem.*, **18**, 243 (1969).

(22) S. Scavnicar, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **118**, 248 (1963).

(23) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(24) S. C. Jain and R. Rivest, *Can. J. Chem.*, **47**, 2209 (1969).

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

(26) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 260–264.