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The Crystal Structure of Bis(Ethylenediammoniummonobromide)tetrabromocuprate(II)

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The compounds ethylenediammoniumtetrabromocuprate(II), $(NH_3CH_2CH_2NH_3)CuBr_4$ and bis(ethylenediammoniummonobromide)tetrabromocuprate(II), $(NH_3CH_2CH_2NH_2 . HBr)_2CuBr_4$ were prepared and the structure of the latter compound determined by the multiple film X-ray diffraction technique. This compound crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.78$ A, $b = 20.15$ A, $c = 6.33$ A, $\beta = 94.9°$, and $Z = 2$ ($\rho_{calc} = 2.57$, $\rho_{obs} = 2.55$). Refinement by least squares on 944 reflections led to a final R of 10.9%. Four bromine atoms surround each copper atom in a very distorted compressed tetrahedral configuration at distances of 2.340(±0.003) to 2.450(±0.010) while the unique angles are 141.1(±0.3), 100.7(±0.2), 99.0(±0.2) and 118.1(±0.3). The ethylenediammonium ions are hydrogen bonded to the $CuBr_4^{2-}$ ions and the remaining two bromine atoms. The compound $(NH_3CH_2CH_2NH_3)CuBr_4$ is isomorphous to the corresponding chloro complex and thus contains square planar $CuBr_4^{2-}$ ions.

Introduction

As a part of a continuing study of the coordination of copper(II) halide complexes, the preparation of the bromo complex[1] analogous to the ethylenediammonium tetrachlorocuprate(II) compound was attempted. In addition to deep red plate type crystals of the expected compound $(enH_2)CuBr_4$, dark red needle crystals with a stoichiometry corresponding to the empirical formula $(enH_2)_2CuBr_6$ were obtained (en = $NH_2CH_2CH_2NH_2$). Since an octahedrally coordinated species had been suggested for the corresponding cobalt(II) analogue $(enH_2)_2CoCl_6$ [2,3] a three-dimensional X-ray diffraction study was undertaken to determine the coordination of the copper(II) species.

Preparation and Data Collection

The compounds $(enH_2)CuBr_4$ and $(enH . HBr)_2CuBr_4$ were prepared by evaporation of an alcohol solution of $CuBr_2$ containing en . 2HBr in excess. The tetrabromo species crystallizes as flat plates while the complex with a formal stoichiometry of a hexabromo species crystallizes as long prismatic needles. Later preparations of $(enH . HBr)_2CuBr_4$ were made at 50°C from a 1:1 alcohol-water solution with a ratio of 1.25 en . 2HBr to $CuBr_2$.[4]. Samples were separated by mineralogical flotation (tetrabromomethane diluted with carbon tetrachloride).

Anal. Calculated for $(enH . HBr)_2CuBr_4$: Cu, 9.53; N, 8.40; C, 7.19; H, 3.02; Br, 71.9. Found: Cu, 9.62; N, 8.27; C, 7.17; H, 2.86; Br, 72.09.

The lattice constants for the monoclinic unit cell of $(enH_2)CuBr_4$, determined from Weissenberg photographs (Cu K_α and K_β radiation) exposed at 20°C, are $a = 8.22 \pm 0.02$ A, $b = 7.71 \pm 0.02$ A, $c = 7.42 \pm 0.01$ A, and $\beta = 92.12 \pm 0.05°$.[5] Systematic extinctions [$\ell = 2n+1$ for $h0\ell$ reflections and $k = 2n+1$ for $0k0$ reflections] imply the space group $P2_1/c$. The observed density is greater than 2.96 g/cc since the crystals sink in tetrabromomethane. The calculated density for $Z = 2$ is 3.22 g/cc. The lattice constants are nearly identical to those for the corresponding chloro complex[6] as shown in Table I. Because of this isomorphism of the two compounds, and since the CuX_4^{2-} ion sits on a center of symmetry in the space group $P2_1/c$, it is reasonable to conclude that the bromo complex contains a square planar $CuBr_4^{2-}$ ion.

Table I. Lattice Constants for $(enH_2)CuX_4$ Compounds

	$(enH_2)CuBr_4$	$(enH_2)CuCl_4$ [a]
a	8.22	8.11
b	7.77	7.37
c	7.42	7.19
β	92.12	92.46
Space Gr.	$P2_1/_c$	$P2_1/_c$

[a] Ref. 6.

The lattice constants for $(enH . HBr)_2CuBr_4$, determined from Weissenberg photographs (Cu K_α and K_β radiation) exposed at 20°C, are $a = 6.78 \pm 0.01$ A, $b = 20.15 \pm 0.01$ A, $c = 6.33 \pm 0.01$ A and $\beta = 94.92 \pm 0.10°$.[5] Systematic extinctions [$k = 2n+1$ for $0k0$ reflections] were observed on the Weissenberg films of 0kl indicating the space groups $P2_1$ or $P2_1/m$. The observed density is 2.55±0.03 g/cc

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(1) J. V. Dubsky and V. Dostal, *Publ. Faculte Sci. Univ. Masaryk*, *160*, 1 (1932).
(2) M L. Schultz, *J. Am. Chem. Soc.*, *71*, 1288 (1949).
(3) Meyer and K. Hoehne, *Z. Anorg. Allgem. Chem.*, *222*, 161 (1935).

(4) Our thanks to M. Moustafa for the refined preparation.
(5) Errors are the standard deviations for measurement of 8-14 pairs of axial reflections.
(6) G B. Birrell, G. L. Ferguson, and B. Zaslow, paper E-4, 1968 Winter Meeting of American Crystallographic Association, Tuscon, Arizona.

Table II. Parameters for $(EnH . HBr)_2CuBr_4$ [a, b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.3983(10)	0.2500	0.3112(6)	0.0289(37)	0.0019(1)	0.0297(11)	0.0	0.0020(14)	0.0
Br(2)	0.3098(5)	0.1405(1)	0.2244(3)	0.0404(26)	0.0021(1)	0.0323(6)	—0.0009(2)	0.0006(9)	—0.0010(1)
Br(3)	0.7459(9)	0.2500	0.2340(5)	0.0323(35)	0.0037(1)	0.0320(9)	0.0	0.0027(12)	0.0
Br(4)	0.8012(5)	0.0065(1)	0.2598(3)	0.0301(23)	0.0026(1)	0.0245(5)	0.0003(2)	—0.0040(8)	0.0000(1)
Br(5)	0.3253(7)	0.2500	0.6797(4)	0.0331(30)	0.0023(1)	0.0251(7)	0.0	—0.0003(10)	0.0
N(6)	0.6835(46)	0.0320(10)	0.7610(31)	0.0403(142)	0.0033(6)	0.0453(69)	0.0016(21)	0.0016(72)	—0.0025(15)
C(7)	0.6541(59)	0.1043(12)	0.7551(43)	0.0429(166)	0.0024(5)	0.0617(102)	—0.0013(27)	—0.0413(105)	0.0026(18)
C(8)	0.8478(62)	0.1395(11)	0.7687(34)	0.0560(175)	0.0030(6)	0.0288(55)	0.0036(26)	0.0091(74)	—0.0009(14)
N(9)	0.9636(50)	0.1378(9)	0.5817(36)	0.0568(156)	0.0030(5)	0.0495(75)	—0.0008(21)	0.00126(81)	—0.0022(15)

$R_1 = \sum_{hkl} ||F_{obs}| - |F_{calc}|| / \sum_{hkl} |F_{obs}| = 0.11$. For Observed Reflections. [a] Estimated standard deviation of the final digits are given in parentheses. [b] The β_{ij} are defined by $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{12}hk - 2\beta_{13}h\ell - 2\beta_{23}k\ell)$.

(flotation in a carbon tetrachloride-carbon tetrabromide mixture) while the calculated density is 2.57 g/cc for Z = 2.

Intensity data for $(enH . HBr)_2CuBr_4$ were collected on a Weissenberg camera using Cu K_α radiation and a Ni filter. The crystal used was 0.02 cm long (parallel to the <100> direction) by 0.008 cm (square cross-section). The linear absorption coefficient was 199 cm^{-1}. No absorption corrections were applied. The zero through third layers were collected while rotating about the <100> direction (needle axis) and a zero layer was collected while rotating about the <010> direction. From these layers 944 observed reflections were recorded, of which 895 were unique. The intensities were estimated visually and reduced to structure factors with associated weights for subsequent least square analysis.[7]

Determination of Structure

The locations of the copper and bromine atoms were determined from study of two- and three-dimensional Patterson functions.[8] The space group $P2_1/m$ was assumed and substantiated by the successful structure solution. These positions were refined by least squares analysis.[9] When a value of R_1 (see Table II for definition of R_1) below 0.20 was obtained, the positions of the carbon and nitrogen atoms were obtained by a difference Fourier synthesis.[8] The final refinement with anisotropic temperature factors was car-

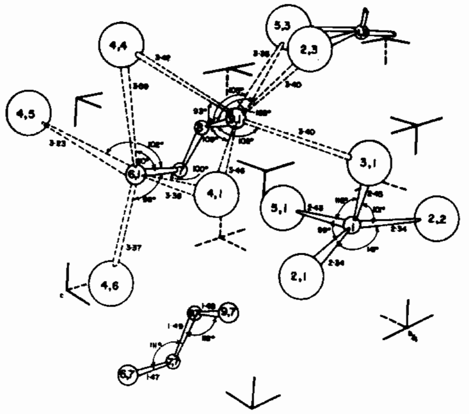

Figure 1. $(enH . HBr)_2CuBr_4$ from the <141> direction showing 1/4 of the unit cell and major interatomic distances and bond angles. The atoms are labeled as shown in Table IV.

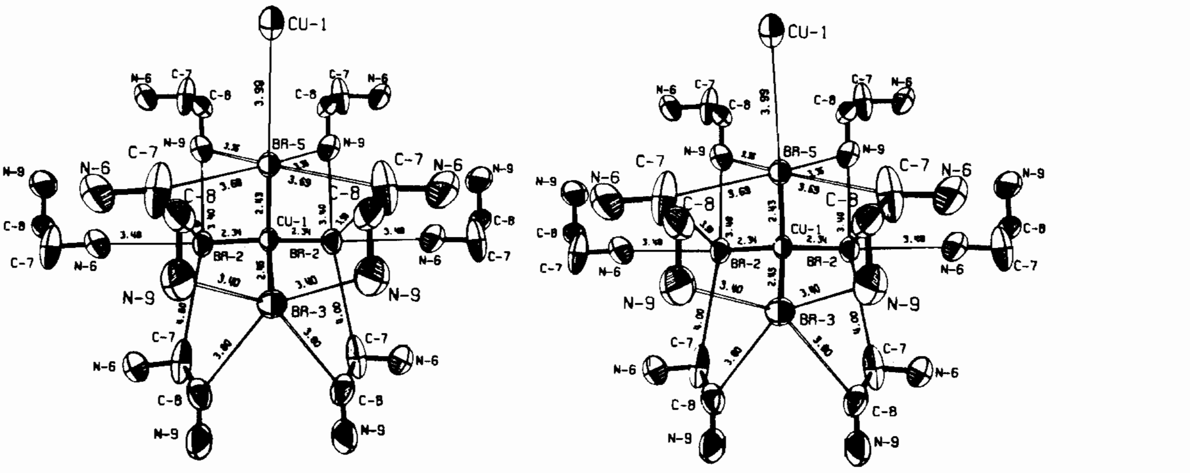

Figure 2. $(enH . HBr)_2CuBr_4$ viewed parallel to the mirror plane at y = 1/4 showing the $CuBr_4^{2-}$ ion and its environment to a distance of 4.00 Å. All atoms within 4.00 Å of the ion are shown connected by slim « bonds » to the bromine.

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(7) D. N. Anderson, Ph. D. Thesis, Washington State University, 1970 For the weighting scheme employed see R. D. Willett, C. Dwiggens Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, *38*, 2429 (1963).

(8) W. G. Sly, D. P Shoemaker, and J. H. Van den Hende, ESSO Research and Engineering Company Report CBRL-22M-62 (1962).

(9) W. R. Busing, K. O. Martin, and H. A. Levy, U. S. Atomic Energy Commission Report ORNL-TM-305 (1962).

Table III. Observed and Calculated Structure Factors For $(EnH . HBr)_2CuBr_4$ [a]

K	L	FO	FC
H = 0			
0	1	453	-431
0	2	3416	-3463
0	3	269	289
0	4	1387	1314
0	5	-67	-28
0	6	337	-360
0	7	106	-66
0	8	69	74
1	1	1057	-1083
1	2	529	-541
1	3	890	871
1	4	354	356
1	5	377	-387
1	6	184	-193
1	7	127	136
1	8	58	50
2	0	476	-527
2	1	294	299
2	2	67	80
2	3	308	-332
2	4	363	348
2	5	47	28
2	6	379	-334
2	7	150	114
2	8	193	144
3	1	278	205
3	2	53	51
3	3	55	-75
3	4	90	-103
3	5	131	110
3	6	-49	10
3	7	83	-58
4	0	1097	1326
4	1	373	-427
4	2	1114	-1079
4	3	1052	968
4	4	349	315
4	5	543	-575
4	6	-49	-22
4	7	208	161
5	1	217	293
5	2	179	195
5	3	174	-172
5	4	80	-87
5	5	82	-88
5	6	122	112
5	7	88	76
6	0	290	283
6	1	292	301
6	2	375	-343
6	3	528	-566
6	4	531	522
6	5	229	237
6	6	479	-369
6	7	48	14
7	1	169	177
7	2	208	223
7	3	267	-204
7	4	193	-185
7	5	127	133
7	6	123	87
7	7	58	-57
8	0	2836	3026
8	1	281	-312
8	2	2058	-2046
8	3	332	327
8	4	802	837
8	5	100	-97
8	6	260	-230
8	7	44	-24
9	1	1068	-1153
9	2	361	-359
9	3	979	907
9	4	273	261
9	5	405	-422
9	6	153	-143
9	7	175	151
10	0	975	-1103
10	1	149	147
10	2	563	574
10	3	53	-58
10	4	-47	-2
10	5	110	-110
10	6	217	-157
10	7	186	135
11	1	269	246
11	2	233	246
11	3	153	-163
11	4	228	-246
11	5	75	71
11	6	138	125
11	7	-36	-17
12	0	948	992
12	1	230	-234
12	2	741	-739
12	3	449	466
12	4	219	239
12	5	331	-271
12	6	-51	-15
12	7	71	64
13	1	64	62
13	2	92	101
13	3	-47	-20
13	4	61	-69
13	5	94	-88
13	6	100	83
13	7	-25	61
14	0	264	286
14	1	170	182
14	2	270	-295
14	3	383	-393
14	4	340	355
14	5	268	216
14	6	292	-236
15	1	378	-403
15	2	-47	-10
15	3	221	247
15	4	-59	-3
15	5	84	-67
15	6	-40	-16
16	0	756	803
16	1	156	-171
16	2	577	-575
16	3	275	285
16	4	245	217
16	5	201	-147
16	6	-35	-47
17	1	513	-562
17	2	106	-102
17	3	447	452
17	4	91	69
17	5	296	-241
17	6	33	-29
18	0	588	-596
18	1	61	62
18	2	390	364
18	3	58	-30
18	4	83	-68
18	5	70	-51
19	1	100	98
19	2	172	168
19	3	91	-80
19	4	173	-166
19	5	-37	24
20	0	654	581
20	1	80	-69
20	2	525	-420
20	3	114	109
20	4	178	152
20	5	50	-47
21	1	124	-121
21	2	-53	-6
21	3	100	93
21	4	-38	7
22	0	106	97
22	1	85	66
22	3	173	-140
22	4	136	136
23	1	299	-265
23	2	-43	-24
23	3	206	178
24	0	93	90
24	1	85	-72
24	2	51	-56
24	3	126	142
25	1	113	-101
25	2	-25	2
26	0	81	-154
H = 1			
0	0	852	-610
0	1	289	334
0	-1	356	-370
0	2	-37	32
0	-2	1230	1038
0	3	560	-517
0	-3	-45	50
0	4	533	484
0	-4	521	-490
0	5	209	223
0	-5	-64	-67
0	6	364	-373
0	-6	-90	93
0	7	-70	-34
0	-7	128	123
0	8	89	132
0	-8	-42	-10
1	1	904	705
1	-1	292	-266
1	2	369	387
1	-2	468	464
1	3	560	-512
1	-3	195	-212
1	4	62	-38
1	-4	187	168
1	5	209	220
1	-5	58	40
1	6	133	-122
1	-6	207	-214
1	7	-62	0
1	-7	-64	45
1	-8	82	89
2	1	106	94
2	-1	526	-535
2	2	665	-624
2	-2	656	-660
2	3	-42	5
2	-3	783	762
2	4	206	205
2	-4	96	101
2	5	128	129
2	-5	505	-493
2	6	101	-87
2	-6	126	122
2	7	155	-130
2	-7	222	181
2	-8	107	-92
3	0	264	197
3	1	502	-440
3	-1	428	-464
3	2	116	106
3	-2	87	68
3	3	812	739
3	-3	666	646
3	4	400	-405
3	-4	180	-210
3	5	393	-376
3	-5	384	-402
3	6	292	264
3	-6	162	182
3	7	126	106
3	-7	116	106
3	-8	53	-56
4	0	193	-167
4	1	3395	3113
4	-1	2699	-2343
4	2	209	-210
4	-2	290	-264
4	3	2029	-1888
4	-3	1232	1126
4	4	201	213
4	-4	410	422
4	5	857	781
4	-5	466	-491
4	6	125	-104
4	-6	292	-290
4	7	276	-215
4	-7	194	158
4	-8	96	131
5	0	1001	935
5	1	54	-24
5	-1	1034	1004
5	2	1057	-931
5	-2	937	-873
5	3	523	-570
5	-3	918	-945
5	4	814	820
5	-4	536	509
5	5	328	320
5	-5	588	561
5	6	485	-403
5	-6	327	-275
5	7	100	-97
5	-7	201	-159
5	-8	64	77
6	0	925	820
6	1	621	-555
6	-1	92	-46
6	2	600	-600
6	-2	243	-254
6	3	368	365
6	-3	377	414
6	4	298	330
6	-4	177	-181
6	5	60	-47
6	-5	372	-352
6	6	213	-184
6	-6	292	234
6	7	97	-66
6	-7	188	162
7	0	554	547
7	1	493	-521
7	-1	62	-58
7	2	228	-238
7	-2	343	-353
7	3	614	604
7	-3	327	382
7	4	-56	-64
7	-4	-55	-28
7	5	291	-325
7	-5	188	-210
7	6	121	116
7	-6	121	98
7	7	84	82
7	-7	-57	35
8	0	344	-350
8	1	612	655
8	-1	495	-550
8	2	-43	-18
8	-2	604	564
8	3	589	-583
8	-3	225	181
8	4	317	341
8	-4	251	-262
8	5	236	235
8	-5	88	-80
8	6	319	-260
8	-6	71	25
8	7	52	-38
8	-7	101	90
9	0	456	-508
9	1	462	459
9	-1	237	-232
9	2	267	279
9	-2	282	295
9	3	235	-294
9	-3	80	-82
9	4	58	-30
9	-4	185	190
9	5	84	95
9	-5	60	-31
9	6	139	-103
9	-6	244	-212
9	7	68	43
9	-7	64	65
10	0	655	704
10	1	638	659
10	-1	724	-817
10	2	362	-401
10	-2	699	-722
10	3	332	-338
10	-3	786	775
10	4	-59	28
10	-4	308	308
10	5	217	232
10	-5	402	-434
10	6	-66	29
10	-6	-67	-22
10	7	140	-134
10	-7	148	133
11	0	681	746
11	1	429	-456
11	-1	105	112
11	2	409	-475
11	-2	416	-477
11	3	416	455
11	-3	112	137
11	4	82	89
11	-4	73	61
11	5	233	-223
11	-5	77	-83
11	6	64	51
11	-6	65	61
11	7	56	48
11	-7	-45	4
12	0	100	-115
12	1	1299	1269
12	-1	869	-949
12	2	113	-104
12	-2	53	16
12	3	845	-902
12	-3	439	481
12	4	178	191
12	-4	123	125
12	5	485	390
12	-5	220	-210
12	6	130	-113
12	-6	148	-126
12	7	90	-108
12	-7	95	91
13	0	576	586
13	1	98	-73
13	-1	485	530
13	2	634	-616
13	-2	500	-565
13	3	192	-226
13	-3	500	-546
13	4	542	549
13	-4	353	389
13	5	115	128
13	-5	369	323
13	6	300	-285
13	-6	260	-213
14	0	323	344
14	1	462	-476
14	-1	120	138
14	2	235	-276
14	-2	57	-41
14	3	317	338
14	-3	106	117
14	4	155	185
14	-4	158	-178
14	5	110	-95
14	-5	193	-152
14	6	129	-119
14	-6	197	173
15	0	105	112
15	1	168	-208
15	-1	189	-211
15	2	-59	21
15	-2	72	-75
15	3	335	399
15	-3	337	364
15	4	124	-133
15	-4	-73	3
15	5	295	-255
15	-5	278	-236
15	6	89	91
15	-6	-50	19
16	0	95	-103
16	1	616	594
16	-1	384	-447
16	2	-60	-14
16	-2	92	97
16	3	410	-450
16	-3	146	181
16	4	121	108
16	-4	-71	5
16	5	197	182
16	-5	79	-50
16	6	81	-80
16	-6	63	-51
17	0	143	-161
17	1	146	168
17	-1	60	-35
17	2	61	70
17	-2	74	68
17	3	138	-142
17	-3	73	-78
17	4	-68	34
17	-4	121	111
17	5	56	50
17	-5	-57	15
17	-6	99	-110
18	0	292	332
18	1	318	347
18	-1	388	-411
18	2	140	-171
18	-2	331	-362
18	3	176	-201
18	-3	446	383
18	4	-64	-8
18	-4	194	184
18	5	127	130
18	-5	274	-217
19	0	451	505
19	1	108	-226
19	-1	125	136
19	2	438	-381
19	-2	402	-361
19	3	175	181
19	-3	68	-28
19	4	163	164
19	-4	101	100
19	5	79	-82
19	-5	-45	28
20	0	129	-116
20	1	189	196
20	-1	117	-117
20	2	-70	-20
20	-2	144	143
20	3	177	-167
20	-3	-64	31
20	4	119	106
20	-4	69	-56
21	0	121	110
21	1	-69	-16
21	-1	127	129
21	2	136	-142
21	-2	135	-140
21	3	58	-46
21	-3	138	-140
21	4	119	166
21	-4	146	143
22	0	100	90
22	1	203	-204
22	-1	102	92
22	2	59	-53
22	-2	-59	-15
22	3	155	151
22	-3	-51	9
22	-4	-36	-58
23	0	-59	19
23	1	73	-60
23	-1	129	-109
23	2	-52	29
23	-2	-52	-15
23	3	126	154
23	-3	133	164
24	0	-52	-17
24	1	285	266
24	-1	177	-190
24	2	-43	5
24	-2	-43	-21
25	-1	38	43
H = 2			
0	0	2984	-2340
0	1	1269	1138
0	-1	1915	-1452
0	2	2420	2026
0	-2	2063	1744
0	3	670	-795
0	-3	926	958
0	4	936	-976
0	-4	762	-813
0	5	279	347
0	-5	422	-476
0	6	313	328
0	-6	183	263
0	7	87	-101
0	-7	224	216
0	-8	67	-94
1	1	308	365
1	-1	1168	-932
1	2	363	-373
1	-2	1490	-1233
1	3	81	-119
1	-3	860	810
1	4	280	-292
1	-4	596	624
1	5	163	209
1	-5	354	-450
1	6	230	238
1	-6	-88	-127
1	7	153	-145
1	-7	97	102
1	-8	-48	-2
2	0	52	-128
2	1	719	710
2	-1	696	-604
2	2	-47	37
2	-2	214	237
2	3	517	-476
2	-3	240	258
2	4	81	-86
2	-4	223	-271
2	5	315	297
2	-5	-86	-20
2	6	110	94
2	-6	137	186
2	7	158	-166
2	-7	-90	-51
2	-8	55	-69
3	0	363	-464
3	1	491	502
3	-1	66	120
3	2	57	-80
3	-2	485	518
3	3	454	-478
3	-3	630	-635
3	4	312	327
3	-4	-77	-34
3	5	112	166
3	-5	362	416
3	6	213	-223
3	-6	-107	-121
3	7	-80	17
3	-7	105	-128
3	-8	43	68
4	0	877	-878
4	1	297	315
4	-1	203	194
4	2	371	354
4	-2	753	709
4	3	357	-361
4	-3	146	-213
4	4	108	-122
4	-4	378	-443
4	5	328	317
4	-5	-87	56
4	6	-101	3
4	-6	243	266
4	7	167	-166
4	-7	-87	-1
4	-8	61	-118
5	0	-36	15
5	1	767	-766
5	-1	121	108
5	2	234	222
5	-2	104	-122
5	3	617	640
5	-3	654	641
5	4	258	-245
5	-4	165	-209
5	5	205	-254
5	-5	399	-481
5	6	157	135
5	-6	197	211
5	7	-76	10
5	-7	147	184
6	0	389	-400
6	1	494	599
6	-1	867	-789
6	2	443	455
6	-2	443	400
6	3	358	-386
6	-3	538	511
6	4	304	-316
6	-4	290	-288
6	5	180	191
6	-5	124	-172
6	6	178	180
6	-6	124	134
6	7	96	-96
6	-7	-83	18
7	0	462	-575
7	1	198	271
7	-1	255	222
7	2	-59	-1
7	-2	565	591
7	3	297	-293
7	-3	481	-474
7	4	329	333
7	-4	172	-216
7	5	-86	42
7	-5	244	308
7	6	232	-229
7	-6	-103	-18
7	7	-70	53
7	-7	-80	-77
8	0	1534	-1368
8	1	742	651
8	-1	813	-752
8	2	1319	1225
8	-2	1196	1080
8	3	614	-527
8	-3	553	534
8	4	738	-632
8	-4	556	-554
8	5	215	269
8	-5	215	-293
8	6	203	215
8	-6	182	200
8	7	70	-89
8	-7	132	144
9	0	1422	1208
9	1	478	492
9	-1	970	-869
9	2	548	-507
9	-2	1250	-1080
9	3	300	-264
9	-3	761	733
9	4	90	-81
9	-4	595	582
9	5	222	253
9	-5	355	-407
9	6	149	118
9	-6	117	-142
9	7	129	-146
9	-7	86	102
10	0	269	274
10	1	244	216
10	-1	-68	21
10	2	309	-363
10	-2	-73	-85
10	3	226	-227
10	-3	107	-125
10	4	133	156
10	-4	103	-112
10	5	234	206
10	-5	104	128
10	6	-89	-15
10	-6	165	137
10	7	116	-135
10	-7	79	-90
11	0	545	-506
11	1	121	135
11	-1	151	163
11	2	-73	-2
11	-2	601	558
11	3	139	-157
11	-3	323	-312
11	4	333	304
11	-4	197	-233
11	5	-102	10
11	-5	191	183
11	6	235	-223
11	-6	-92	8
11	-7	-60	-25
12	0	570	-527
12	1	160	185
12	-1	-76	-12
12	2	330	340
12	-2	412	428
12	3	179	-215
12	-3	-85	-30
12	4	140	-147
12	-4	211	-240
12	5	168	165
12	-5	-105	-14
12	6	-80	26
12	-6	127	125
13	0	111	109
13	1	339	-331
13	-1	85	-50
13	2	-80	55
13	-2	129	-125
13	3	336	322
13	-3	389	430
13	4	102	-108
13	-4	88	-91
13	5	136	-131
13	-5	348	-329
13	6	74	62
13	-6	149	123
14	0	315	-301
14	1	312	322
14	-1	477	-483
14	2	365	357
14	-2	237	274
14	3	159	-187
14	-3	356	369
14	4	238	-251
14	-4	151	-180
14	5	-92	69
14	-5	130	-149
14	6	124	136
14	-6	-76	66
15	0	-81	17
15	1	582	519
15	-1	184	-229
15	2	159	-175
15	-2	94	14
15	3	428	-435
15	-3	89	-98
15	4	264	222
15	-4	113	99
15	5	182	177
15	-5	153	118
15	6	121	-133
15	-6	106	-104
16	0	385	-370
16	1	138	152
16	-1	94	-87
16	2	267	303
16	-2	319	319
16	3	219	-189
16	-3	-88	52
16	4	156	-153
16	-4	197	-196
16	5	155	135
16	-5	-87	-47
16	-6	69	94
17	0	753	576
17	1	190	206
17	-1	399	-392
17	2	348	-307
17	-2	579	-505
17	3	110	-110
17	-3	444	388
17	4	-92	41
17	-4	333	254
17	5	128	114
17	-5	290	-236
17	-6	41	-54
18	0	181	192
18	1	-86	-4
18	-1	126	99
18	2	244	-229
18	-2	-107	-89
18	3	-98	-29
18	-3	152	-118
18	4	134	114
18	-4	-91	-20
18	5	62	57
18	-5	84	89
19	0	352	-254
19	1	-104	30
19	-1	-106	63
19	2	-101	-1
19	-2	400	296
19	3	-93	-30
19	-3	118	-86
19	4	163	166
19	-4	175	-164
19	5	-45	-27
19	-5	84	41
20	0	383	-284
20	1	118	126
20	-1	133	-119
20	2	338	248
20	-2	215	201
20	3	86	-100
20	-3	96	87
20	4	126	-127
20	-4	87	-86
20	-5	46	-56
21	0	195	161
21	1	-94	-14
21	-1	95	-116
21	2	-88	-48
21	-2	189	-159
21	3	-76	46
21	-3	254	202
21	4	-53	-28
21	-4	116	41
22	0	117	-107
22	1	114	122
22	-1	191	-174
22	2	139	119
22	-2	96	105
22	3	65	-71
22	-3	144	134
23	0	94	73
23	1	338	273
23	-1	173	-161
23	2	113	-106
23	-2	-70	-61
24	0	-67	-23
24	1	-63	-5
24	-1	-64	59
24	2	-50	-7
24	-2	-54	35
25	0	126	141
25	1	-39	-1
25	-1	57	-73
H = 3			
0	0	815	743
0	1	1069	-954
0	-1	905	743
0	2	-55	-3
0	-2	638	-656
0	3	492	448
0	-3	347	-386
0	4	330	-317
0	-4	132	156
0	5	-85	-75
0	-5	222	249
0	6	311	266
0	-6	-79	61
0	7	-67	-49
0	-7	130	-148
1	1	68	-115
1	-1	267	243
1	2	93	-84
1	-2	822	681
1	3	91	99
1	-3	477	-442
1	4	184	192
1	-4	467	-412
1	5	-85	-90
1	-5	223	272
1	6	97	-104
1	-6	115	154
1	7	-69	56
1	-7	65	-93
2	1	314	416
2	-1	42	-18
2	2	903	696
2	-2	1009	928
2	3	307	-306
2	-3	385	-330
2	4	299	-275
2	-4	301	-346
2	5	-85	60
2	-5	249	271
2	6	97	108
2	-6	-81	18
2	7	-68	36
2	-7	80	-98
3	0	370	712
3	1	292	-323
3	-1	275	258
3	2	462	-375
3	-2	650	-588
3	3	104	97
3	-3	76	-116
3	4	79	108
3	-4	277	278
3	5	85	98
3	-5	-68	-7
3	6	-96	-60
3	-6	-81	-29
4	0	497	-683
4	1	1514	-1367
4	-1	1424	1068
4	2	938	718
4	-2	468	480
4	3	1302	1067
4	-3	440	-388
4	4	724	-630
4	-4	479	-405
4	5	367	-433
4	-5	-69	62
4	-6	306	300
5	0	1085	-996
5	1	1000	923
5	-1	907	-877
5	2	993	661
5	-2	785	708
5	3	578	-454
5	-3	574	559
5	4	221	-281
5	-4	304	-325
5	5	-85	48
5	-5	135	-187
5	-6	-80	36
6	0	754	-685
6	1	668	565
6	-1	169	-147
6	2	567	488
6	-2	521	526
6	3	588	-522
6	-3	257	-304
6	4	167	-199
6	-4	128	-140
6	-5	288	316
7	0	285	341
7	1	-52	16
7	-1	59	-85
7	2	-62	-65
7	-2	470	-434
7	3	90	-96
7	-3	184	205
7	4	-83	-57
7	-4	203	220
7	-5	129	-159
8	0	378	330
8	1	1088	-773
8	-1	667	588
8	2	134	109
8	-2	268	-327
8	3	382	425
8	-3	253	-270
8	4	186	-287
8	-4	-67	42
8	-5	134	151
9	0	260	-279
9	1	-61	-55
9	-1	162	164
9	2	69	-64
9	-2	543	563
9	3	-79	28
9	-3	346	-332
9	4	85	159
9	-4	333	-376
9	-5	249	213
10	0	1236	-1069
10	1	81	95
10	-1	81	113
10	2	666	613
10	-2	1089	914
10	3	-81	-17
10	-3	207	-238
10	-4	336	-400
10	-5	146	145
11	0	137	140
11	1	138	164
11	-1	235	-237
11	2	-76	75
11	-2	246	-255
11	3	101	-153
11	-3	287	269
11	-4	129	147
11	-5	184	-172
12	0	279	-210
12	1	771	-701
12	-1	549	526
12	2	306	338
12	-2	127	132
12	-3	197	-201
12	-4	134	-167
12	-5	-78	51
13	0	716	-553
13	1	753	651
13	-1	615	-595
13	2	326	370
13	-2	479	435
13	-3	332	373
13	-4	196	-222
13	-5	147	-135
14	0	220	-227
14	1	326	366
14	-1	82	-117
14	2	103	168
14	-2	139	169
14	-3	135	-165
14	-4	-81	-14
14	-5	169	196
15	0	207	230
15	1	103	-116
15	-1	96	120
15	2	85	-139
15	-2	140	-171
15	-3	-68	-45
15	-4	-79	46
15	-5	-67	-17
16	0	-85	-17
16	1	377	-426
16	-1	276	287
16	-2	-69	-8
16	-3	82	-77
16	-4	-75	-59
17	0	167	-186
17	-1	-69	3
17	-2	331	285
17	-3	97	-95
17	-4	156	-190
18	-1	82	63
18	-2	590	442
18	-3	92	-111
18	-4	208	-204
19	-1	197	-218
19	-2	-76	-57
19	-3	263	226
20	-1	139	125
20	-2	87	-96
21	-1	134	-169
21	-2	142	161
H = 4			
0	0	165	165
0	-1	928	808
0	-2	102	122
0	-3	783	-811
0	4	286	440
0	-4	82	-83
0	5	293	-323
0	-5	453	544
0	6	159	-184
0	-6	-75	-56
0	7	-15	168
0	-7	238	-201
H = 5			
0	0	87	83
0	1	73	104
0	-1	261	-283
0	2	-76	49
0	-2	179	-225
0	3	-78	-32
0	-3	363	382
0	4	-92	-2
0	-4	173	210
0	5	-79	-16
0	-5	301	-281
0	6	-52	-42
0	-6	168	-128
0	-7	161	142
H = 6			
0	0	162	153
0	1	274	248
0	-1	319	-280
0	2	-77	-54
0	-2	191	-181
0	3	210	-206
0	-3	249	262
0	4	-78	15
0	-4	106	91
0	5	130	133
0	-5	175	-156
H = 7			
0	0	-90	-67
0	1	-88	70
0	-1	-79	-27
0	2	-82	-44
0	-2	203	183
0	3	-71	-45
0	-3	-73	-57
0	4	-50	52
0	-4	253	-177
0	-5	106	87
H = 8			
0	0	140	-109
0	1	87	-83
0	-1	116	106
0	2	129	131

[a] The columns list k, ℓ, $10|F_{obs}|$, and $10 F_{calc}$. Unobserved reflections are denoted by a negative $10|F_{obs}|$.

ried to a value of $R_1 = 0.11$ for the observed reflections and 0.13 for all reflections.[10] Unobserved reflections were omitted from the refinement if the calculated structure factor was less than F_{min} the structure factor corresponding to the minimum observable

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(10) Atomic scattering factors, (corrected for the real component of the anomalous dispersion term in the case of the Cu and Br atoms) were obtained from: International Tables for X-ray Crystallography Vol. III, 202-207, 214.

Table IV. Interatomic Distances and Angles for $(EnH \cdot HBr)_2CuBr_4$ [a]

Distances and angles in the $CuBr_4^{2-}$ and enH_2^{2+} ions					
Cu(1,1)—Cu(1,8)	10.420(05)	Br(2,1)—Br(3,1)	3.686(07)	Br(2,1)—Cu(1,1)—Br(2,2)	141.1(0.3)
Cu(1,1)—Br(2,1)	2.340(03)	Br(2,1)—Br(5,1)	3.624(05)	Br(2,1)—Cu(1,1)—Br(3,1)	100.7(0.2)
Cu(1,1)—Br(3,1)	2.447(10)	Br(3,1)—Br(5,1)	4.179(06)	Br(2,1)—Cu(1,1)—Br(5,1)	99.0(0.2)
Cu(1,1)—Br(5,1)	2.426(06)	N(6,1)—C(7,1)	1.470(31)	Br(3,1)—Cu(1,1)—Br(5,1)	118.1(0.3)
Cu(1,1)—Br(4,1)	5.637(05)	C(7,1)—C(8,1)	1.489(60)	N(6,1)—C(7,1)—C(8,1)	110.7(3.2)
Br(2,1)—Br(2,2)	4.413(04)	C(8,1)—N(9,1)	1.476(43)	C(7,1)—C(8,1)—N(9,1)	118.0(2.6)
Hydrogen bonding distances and angles					
N(6,1)—Br(2,6)	3.477(31)	C(7,1)—N(6,1)—Br(2,6)	173.0(2,5)	C(8,1)—N(9,1)—Br(2,3)	168.3(2.6)
N(6,1)—Br(4,1)	3.376(21)	C(7,1)—N(6,1)—Br(4,1)	99.8(1.7)	C(8,1)—N(9,1)—Br(3,1)	105.8(2.0)
N(6,1)—Br(4,4)	3.592(30)	C(7,1)—N(6,1)—Br(4,4)	110.1(2.2)	C(8,1)—N(9,1)—Br(4,1)	109.0(2.0)
N(6,1)—Br(4,5)	3.231(22)	C(7,1)—N(6,1)—Br(4,5)	101.8(1.5)	C(8,1)—N(9,1)—Br(4,4)	92.9(2.0)
N(6,1)—Br(4,6)	3.368(31)	C(7,1)—N(6,1)—Br(4,6)	95.6(2.2)	C(8,1)—N(9,1)—Br(5,3)	105.5(2.0)
N(9,1)—Br(2,3)	3.396(31)	Br(4,1)—N(6,1)—Br(2,6)	82.5(0.7)	Br(2,3)—N(9,1)—Br(3,1)	81.0(0.5)
N(9,1)—Br(3,1)	3.403(26)	Br(4,1)—N(6,1)—Br(4,4)	67.9(0.5)	Br(2,3)—N(9,1)—Br(5,3)	64.9(0.6)
N(9,1)—Br(3,5)	5.043(25)	Br(4,1)—N(6,1)—Br(4,5)	146.7(0.9)	Br(3,1)—N(9,1)—Br(5,3)	86.7(0.5)
N(9,1)—Br(4,1)	3.461(23)	Br(4,1)—N(6,1)—Br(4,6)	103.7(0.7)	Br(4,1)—N(9,1)—Br(2,3)	79.8(0.5)
N(9,1)—Br(4,4)	3.425(23)	Br(4,4)—N(6,1)—Br(2,6)	77.0(0.6)	Br(4,1)—N(9,1)—Br(3,1)	91.6(0.7)
N(9,1)—Br(5,1)	4.977(34)	Br(4,4)—N(6,1)—Br(4,5)	80.9(0.6)	Br(4,1)—N(9,1)—Br(4,4)	68.9(0.6)
N(9,1)—Br(5,3)	3.354(30)	Br(4,4)—N(6,1)—Br(4,6)	153.8(0.7)	Br(4,1)—N(9,1)—Br(5,3)	144.6(1.0)
		Br(4,5)—N(6,1)—Br(2,6)	79.2(0.6)	Br(4,4)—N(9,1)—Br(2,3)	83.0(0.6)
		Br(4,5)—N(6,1)—Br(4,6)	99.2(0.7)	Br(4,4)—N(9,1)—Br(3,1)	156.8(1.0)
		Br(4,6)—N(6,1)—Br(2,6)	77.4(0.7)	Br(4,4)—N(9,1)—Br(5,3)	101.7(0.8)
Van der Waals contacts					
Br(2,1)—C(7,1)	3.991(29)	Br(3,5)—C(8,1)	3.802(22)	Br(4,10)—C(7,8)	3.804(35)
Br(2,5)—C(7,1)	3.999(30)	Br(4,1)—C(7,1)	3.904(33)	Br(5,1)—C(7,1)	3.693(31)
Br(2,5)—C(8,7)	4.073(44)	Br(4,5)—C(7,1)	3.813(38)	Br(5,1)—Cu(1,5)	3.986(05)
Br(2,5)—Br(5,1)	4.102(05)	Br(4,8)—Br(4,9)	3.896(05)	Br(5,1)—C(8,7)	4.008(30)
Br(3,1)—C(8,1)	4.061(22)	Br(4,9)—C(8,8)	3.798(24)		

[a] The first subscript refers to the atom in the parameter list and in Figure 1. The second subscript refers to the atom moved according to the following symmetry operations:

1) x, y, z
2) x, ½—y, z
3) 1+x, y, z
4) 2—x, —y, 1—z
5) x, y, 1+z
6) 1—x, —y, 1—z
7) x—1, y, z
8) 1—x, 1—y, 1—z
9) x—1, y+1, z
10) x, y+1, z

intensity. The largest peaks remaining on the difference map after refinement were peaks of 1.8 e/A^3 near bromine atoms and 1.0 e/A^3 near the ethylene-diammonium ion. Final parameters are listed in Table II and the observed and calculated structure factors are given in Table III. Bond distances and angles were computed with the ORFFE program and may be found in Figures 1 and 2, and Table IV.[11] The packing within the unit cell may be seen in Figure 3.

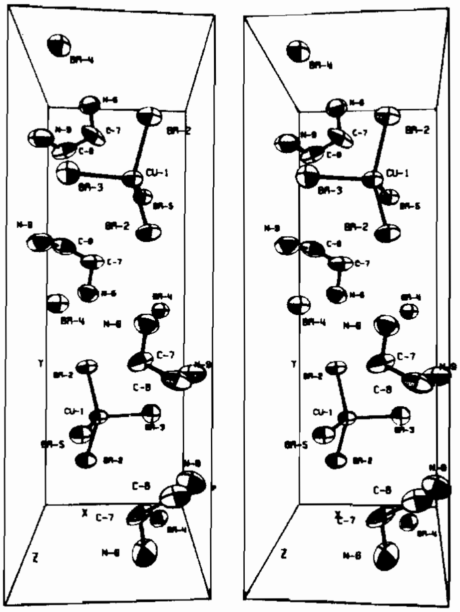

Figure 3. $(enH \cdot HBr)_2CuBr_4$ from the <001> direction showing the packing inside one unit cell.

Discussion

This structure is not close to any regular coordination geometry; however, for purposes of discussion, we will describe it as an extremely distorted tetrahedral $CuBr_4^{2-}$ ion with C_s symmetry as illustrated in Figure 1. The ion contains two short Cu—Br bonds of 2.340(3)A and two longer Cu—Br bonds of 2.426(6) and 2.447(10) A. The shortest distance from the copper ion to the other bromide ions is 5.637 A. The bond angles show considerable deviation from tetrahedral angles with four of the Br—Cu—Br angles compressed in pairs to 99.0° and 100.7°, and the other two angles widened to 118.1° and 141.1°. The tetrabromocuprate ion is thus distorted in a different manner than the corresponding ion in Cs_2CuBr_4.[12] In the

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(11) W. R. Busing, K. O. Martin, and H. A. Lev, U. S. Atomic Energy Commission Report ORNL-TM-306 (1964).
(12) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, *13*, 807 (1960).

Table V. Bond Distances and Angles in Several CuX_4^{2-} ions

	$(enH\,.\,HBr)_2CuBr_4$	Cs_2CuBr_4 [a]	$[(CH_3)_2NH_2]_3CuCl_5$ [b]	Cs_2CuCl_4 [c]
Angles				
	141.1(3)	130.4(4)	136.1(2)	124.9(7)
	118.1(3)	126.4(3)	135.5(2)	123.3(7)
	100.7(2)	101.9(3)	98.6(1)	102.9(7)
	99.0(2)	99.9(3)	97.7(1)	102.5(7)
Distances				
	2.340(3)	2.354(9)	2.229(6)	2.18(3)
	2.340(3)	2.354(9)	2.229(6)	2.18(3)
	2.426(6)	2.380(9)	2.229(9)	2.18(3)
	2.447(10)	2.394(9)	2.232(6)	2.25(3)

[a] Reference 12. [b] M. L. Larsen, Ph D. Thesis, Washington State University (1968). [c] B. Morosin and E. C. Lingafelter, *J. Chem. Phys.*, *65*, 50 (1961).

cesium compound, the corresponding Br–Cu–Br bond angles are 99.9, 101.9, 126.4, and 130.4°, while the bond lengths only vary from 2.35 A to 2.39 A, as shown in Table V. It is interesting to note that the total distortion in the two ions is not much different if one compares the average value of the two compressed angles (99.8 *vs.* 100.4°) and of the two enlarged angles (129.6 *vs.* 128.4°) in the two different compounds. However, the displacement of the center of mass of the bromide ions from the copper ion is much larger in the ethylenediammonium compound (0.238 A) than in the cesium compound (.035 A). This greater displacement is a direct result of the one large Br–Cu–Br bond angle and the difference in the lengths of the two pairs of Cu–Br bond distances.

Examination of the N–Br interatomic distances and the C–N–Br angles reveals several possibilities for N–H ... Br hydrogen bonding in this compound. Nitrogen atom N(6,1) has four close bromide ions, Br(4,5), Br(4,6), Br(4,1) and Br(4,4), at 3.23, 3.37, 3.38 and 3.59 Å and one distance to Br(2,6) of 3.48 Å, with corresponding C–N–Br angles of 101°, 96°, 100°, 110° and 173° respectively (Figure 1). Thus, the first four ions are potential sites for N–H .. Br hydrogen bonding (although the N–Br distance and Br–N–Br angles indicate Br(4,4) is not as favorably located as the other three) and thus the NH_3^+ group is probably disordered. Nitrogen atom (9,1) has five close bromide ions, Br(5,3), Br(2,3) Br(3,1), Br(4,4), and Br(4,1), at 3.35, 3.40, 3.40, 3.42, and 3.46 A respectively. The C–N–Br angles to Br(5,3), Br(3,1), Br(4,4), and Br(4,1) are nearly tetrahedral (105°, 106°, 93°, and 109° respectively) but the angle to Br(2,3) deviates considerably, being nearly linear (168°). Thus, as is revealed by examination of Figure 2, Br(2) is not involved in hydrogen bonding. Again, the hydrogen bonding is probably disordered.

It is of interest to discuss the possible reasons for the large difference between the two « widened » Br–Cu–Br angles in the $CuBr_4^{2-}$ ion since this discrepancy is not observed in other complexes containing distorted CuX_4^{2-} ions. The Br(2)–Cu–Br(2) angle does not appear to be sterically constrained, since all contacts between Br(2) and other atoms are at distances greater than the sum of the van der Waals radii (except for that with N(9) at 3.40 A). In particular, the closest contacts are those which prevent the angle from becoming larger. However, examination of the packing around Br(3) and Br(5) shows that steric restraint determines the Br(3)–Cu–Br(5) angle. Both of these bromine atoms are surrounded by four atoms that « box » it in (Figure 2). Br(5) sits near the center of a square formed by two N(9) atoms (3.35 Å) and two C(7) atoms (3.69 Å). Br(3) sits near the center of a square by two different N(9) atoms (3.40 Å) and two C(8) atoms (3.80 Å). The two squares are joined together by a pair of C(7)–C(8)–N(9) linkages, thus fixing the bromine positions.

In this structure, then, the Br(2)–Cu–Br(2) bond angle of 141.1 is the less sterically hindered value of the two angles which are widened by the distortion from tetrahedral geometry. An idealized $CuBr_4^{2-}$ ion should have four Br–Cu–Br angles of 100° and two of 141°. This is consistent with the trend observed in complexes containing the distorted tetrahedral $CuCl_4^{2-}$ ion. There, as shown by the data in Table V, the « widened » angles are 120° and 136° in Cs_2CuCl_4 and $[(CH_3)_2NH_2]_3CuCl_5$ respectively, as compared with 128° and 141° respectively for Cs_2CuBr_4 and the idealized $CuBr_4^{2-}$ ion in $(enH\,.\,HBr)_2CuBr_4$.

The geometry of CuX_4^{2-} speccics in the solid state depends on many factors, including crystal field stabilization, ligand-ligand repulsions, Jahn-Teller distortions, hydrogen bonding, and van der Waals forces. The role of ligand size is illustrated by examining the ethylenediammoniumcopper halide systems. For the chloride, crystal field stabilization dominates, and only the square-planar ion is formed. (It should also be noted that the structure assumed by that compound provides for efficient hydrogen bonding and packing). In the bromide system, ligand-ligand repulsions increase and offset the crystal field stabilization sufficiently to form the distorted tetrahedral species (although the square-planar species still exists). In order to otbain efficient hydrogen bonding in the structure containing the disorted tetrahedral ion, however, it is necessary to incorporate two bromide ions into the lattice. The effect of ligand-ligand repulsions shows up in the bond distances in the $CuBr_4^{2-}$ ion in $(enH\,.\,HBr)_2CuBr_4$ also. The Br(2)–Cu–Br(2) angle is large, so that the Cu–Br(2) bonds can shorten to 2.34 A and still maintain a Br(2)–Br(2) distance of 4.41 A. With the smaller Br(3)–Cu–Br(5) angle, these Cu–Br distances increase to 2.44 A to offset increased ligand-ligand repulsions. Despite this, the Br(3)–Br(5) distance is only 4.18 A.

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