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The Crystal Structure of Copper(II) Bromide Bis(Dimethylsulphoxide)

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$\{(CH_3)_2SO\}_2CuBr_2$ is isomorphous with the corresponding chloride complex. It belongs to the orthorhombic space group Pnma and contains 4 formula groups per unit cell. The dimensions of the unit cell at ca. *295K are* a = *8.257(2)Å,* b = *11.772(2)Å,* c = *11.749(2)Å. The copper ion assumes an intermediate five-coordinate geometry with three bromine atoms equatorial and two oxygen atoms axial. The equatorial angles are Br(1)–Cu–Br(2) = 146.13° and Br(2)–Cu–Br(2) = 110.21°, and the axial angle O(1)–Cu–O(1′) is 173.99°. The bond lengths are Cu–Br(1) = 2.451(4)Å, Cu–Br(2) = 2.429(4)Å, Cu–Br(2′) = 2.777(4)Å and Cu–O = 1.962(9)Å. The copper coordination geometry is largely determined by packing of the DMSO groups.*

Introduction

As part of a program of structural characterization of copper(II) bromide salts, we have undertaken the crystal structure determination of $CuBr_2 \cdot 2DMSO$. While the structural literature of copper(II) chloride salts is profuse [1], a relatively small number of bromide complexes have been the subject of structural characterization. The distorted (compressed) tetrahedral geometry, as defined in Cs_2CuBr_4 [2], has an average Cu–Br distance of 2.35Å with bond angles near 100° and 125°. This distance is longer (2.39Å) in the more distorted anion present in $(enH_2Br)_2CuBr_4$ [3], indicating this distance is sensitive to distortion. In the distorted (elongated) octahedral geometry, as exemplified in $CsCuBr_3$ [2], the average axial Cu–Br distance is 2.45Å, although the individual distances range from 2.34Å to 2.52Å. The axial distances are 2.87 and 2.96Å. For the trigonal bipyramidal geometry, the axial Cu–Br bond length is 2.45 Å while the equatorial distance is 2.52Å [4, 5]. The bis(dimethylsulfoxide) complex of $CuBr_2$ was chosen for study, since the isomorphous chloride had a coordination geometry intermediate been square pyramidal and trigonal bipyramidal [6]. This, hopefully, would allow the estimation of steric effects in these copper(II) salts which fall in this gray area of five-coordinate geometry intermediate between C_{4v} and D_{3d} symmetry.

Preparation and Data Collection

Small dark brown platelets of $CuBr_2(DMSO)_2$ can be prepared by reacting ethanolic solutions of $CuBr_2$ and DMSO and allowing the slow evaporation of the solvent [7].

Examination of Weissenberg, X-ray diffraction, photographs of a wedge shaped crystal (*ca.* 0.18 X 0.16 X 0.15 mm X 0.01 mm thick) showed it to belong to the orthorhombic class having mmm diffraction symmetry. The lattice constants measured with Zr filtered MoK_α radiation using a Picker diffractometer and single crystal orienter were found to be *a* = 8.257(2)Å, *b* = 11.772(2)Å, and *c* = 11.749(2)Å. Systematic absences for 0kl when k + l = 2n + 1 and for hk0 when h = 2n + 1 suggested that the space group was the same as that found for the corresponding chloride, namely Pnma.

TABLE I. Final Positional and Thermal Parameters[a] for $CuBr_2 \cdot 2DMSO$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	3157(3)	2500	3672(2)	107(5)	18(2)	48(2)	0	110(3)	0
Br(1)	4933(3)	2500	2000(2)	104(4)	43(2)	67(2)	0	340(3)	0
Br(2)	3011(4)	2500	5737(2)	192(6)	42(2)	48(2)	0	–8(3)	0
S	1834(5)	4805(3)	4264(3)	107(7)	25(3)	51(3)	0(4)	19(5)	4(3)
O	3123(13)	4165(7)	3587(8)	116(19)	25(7)	55(9)	20(11)	43(12)	–17(7)
C(1)	3004(26)	5798(15)	5074(20)	240(47)	41(15)	173(26)	–2(23)	–64(32)	–44(17)
C(2)	932(26)	5734(16)	3231(15)	255(48)	57(16)	90(19)	57(23)	–29(26)	2(14)

[a] Parameters multiplied by 10^4.

TABLE II. Interatomic Distance and Angles. Standard Deviation of Last Digit in Parentheses.

	Distance			Angle	
	Cl	Br		Cl	Br
Cooper Coordination Geometry					
Cu–X(1)	2.290(2)	2.451(4)	X(1)–Cu–X(2)	146.1(1)	146.1(2)
Cu–X(2)	2.284(2)	2.429(4)	X(1)–Cu–O	88.7(1)	88.2(3)
Cu–O	1.955(4)	1.962(9)	X(2)–Cu–O	92.9(2)	92.9(3)
			X(1)[a]–Cu–O	87.5(2)	88.4(3)
Cu–X(1)[a]	2.702(2)	2.777(4)	X(1)–Cu–X(1)[a]	112.7(5)	110.2(1)
			X(2)–Cu–X(1)[a]	101.2(1)	103.7(1)
			O–Cu–O	173.0(3)	173.9(6)
			Cu–X(1)[a]–Cu[a]	144.6(1)	
DMSO Geometry					
S–O	1.531(4)	1.53(1)	O–S–C(1)	104.7(3)	102.9(8)
S–C(1)	1.771(7)	1.79(2)	O–S–C(2)	103.9(3)	103.7(7)
S–C(2)	1.765(7)	1.79(2)	C(1)–S–C(2)	100.4(3)	100.7(9)
			Cu–O–S	118.2(2)	118.5(6)
Intermolecular Non-bonded Interactions					
C(1)–Br(1)[b]		3.87(2)			
C(1)–Br(2)		3.96(2)			
C(1)–Br(2)[c]		3.97(2)			
C(2)–Br(2)[d]		3.70(2)			
C(2)–Br(1)[a]		3.90(2)			
C(1)–C(1)		3.80(4)			
Coordination Geometry Non-bonded Interactions					
X(1)–X(2)	4.376(1)	4.668(3)			
X(1)–X(1)[a]	4.161(1)	4.292(3)			
X(2)–X(1)[a]	3.862(1)	4.070(3)			
X(1)–O		3.09(1)			
X(2)–O		3.20(1)			
X(1)[a]–O		3.35(1)			

[a] Atom transformed by −½ + x, ½ − y, ½ − z. [b] Atom transformed by ½ − x, 1 − y, ½ + z. [c] Atom transformed by 1 − x, ½ + y, 1 − z. [d] Atom transformed by ½ − x, 1 − y, −½ + z.

A total of 1024 independent reflections were measured out to $2\theta = 50^\circ$ with Zr filtered MoK_α radiation. A θ–2θ step scan of 2.0° degrees was used with 20 steps/degree and 4 sec/step. Background measurements were made before and after each scan. Absorption corrections ($\mu = 43.9\ \mathrm{cm}^{-1}$) were made. The standard deviation of each reflection was calculated by the expression $\sigma^2(I) = TC + BC + (0.03)^2 I_o^2$ where TC = total counts, BC = background counts, and $I_o = TC - BC$.

The structure was determined by isomorphous substitution of Br for Cl in the structure determined for $CuCl_2(DMSO)_2$. Refinement converged quickly to a final weighted R factor $[\omega_{hkl} = 1/\sigma^2(F)]$ of 0.088 and a conventional R factor of 0.083 for the reflections with $F > 3\sigma(F)$. No attempt was made to find the hydrogen atoms. The final difference map showed no unusual features. The final parameters are reported in Table I and Table II gives pertinent interatomic distances and angles for the Br salt and the isomorphous Cl salt. An illustration of the molecule is given in Fig. 1 while the packing is illustrated in Fig. 2. Computer programs used were part of a local program library [8, 9] containing modified versions of ORFLS3 [10], ALFF [11], ORFFE3 [12], and ORTEP [13].

Discussion

As expected from the isomorphism of $CuCl_2 \cdot 2DMSO$ and $CuBr_2 \cdot DMSO$, the structures of the two salts are virtually identical. In fact, with the exception of the Cu–X (X = Cl, Br) *distances,* the isomorphism is so complete it is unnecessary to comment on many features of the structure.

In the analysis of the properties of $CuCl_2 \cdot 2DMSO$ [6], it was shown that it was more appropriate to

TABLE III. Observed and Calculated Structure Factors for CuBr$_2$·2DMSO. Columns are k, l, 10|F$_o$| and 10F$_c$.

H = 0

K	L	FO	FC
0	2	425	360
0	4	1245	-1355
0	6	531	-501
0	8	891	-835
0	10	0	72
0	12	0	13
1	3	901	985
1	5	1375	1435
1	7	0	-130
1	9	424	-520
1	11	695	-756
1	13	277	320
2	0	1721	-1771
2	2	1023	965
2	4	482	497
2	6	145	-10
2	9	124	144
2	10	263	-251
2	12	310	374
3	1	1185	1051
3	3	1595	-1721
3	5	1202	-1314
3	7	264	317
3	9	232	362
3	11	-571	857
3	13	204	-175
4	2	0	135
4	4	813	-828
4	6	864	-901
4	8	720	-866
4	10	208	159
4	12	0	-10
5	1	1375	-1362
5	3	331	367
5	5	913	925
5	7	0	-93
5	9	335	-325
5	11	471	-528
5	13	0	295
6	0	2821	-2745
6	2	580	544
6	4	718	697
6	6	380	-384
6	8	147	41
6	10	0	-105
6	12	231	267
7	1	945	800
7	3	1112	-1098
7	5	1330	-1343
7	7	90	120
7	9	625	619
7	11	731	748
8	0	1994	2048
8	2	123	15
8	4	566	-570
8	6	565	-569
8	8	421	-476
8	10	180	113
9	1	844	-855
9	3	238	240
9	5	414	409
9	7	126	-100
9	9	182	35
10	0	1245	-1318
10	2	277	275
10	4	344	374
10	6	163	79
10	8	301	200
11	1	397	403
11	3	742	-722
11	5	844	-861
11	7	265	101
12	0	1393	1482
12	2	30	-67
12	4	422	-412
12	6	0	3
13	1	629	-632
13	3	186	-45
13	5	123	335

H = 1

K	L	FO	FC
0	1	-175	-61
0	2	1293	1369
0	3	387	824
0	4	739	-649
0	5	1142	-1176
0	6	935	-928
0	7	957	874
0	9	424	419
0	9	149	-35
0	10	508	496
0	11	293	-311
0	12	257	-167
0	13	157	174
1	1	1690	1771
1	2	445	465
1	3	791	-692
1	4	400	-429
1	5	1250	-1224
1	6	1144	1154
1	7	114	-153
1	8	600	-568
1	9	224	-144
1	10	326	-304
1	11	248	-222
1	12	158	132
1	13	313	296
2	1	644	-580
2	2	1117	1051
2	3	635	-593
2	4	1486	1521
2	5	1290	1348
2	6	973	995
2	7	246	-258
2	8	626	-643
2	9	312	284
2	10	1022	-1089
2	11	0	91
3	13	105	-146
4	1	0	-129
4	2	297	318
4	3	503	485
4	4	329	-268
4	5	941	-897
4	6	570	-557
4	7	620	615
4	8	293	218
4	9	215	-121
4	10	412	434
4	11	121	-190
4	12	0	-60
4	13	171	148
5	1	1647	1615
5	2	444	389
5	3	520	-501
5	4	218	-190
5	5	1138	-1141
5	6	955	954
5	7	374	-312
5	8	545	-547
5	9	292	-204
5	10	329	-306
5	11	147	-149
5	12	233	90
5	1	499	-459
6	2	68	-24
6	3	568	-537
6	4	1322	1335
6	5	1085	1100
6	6	1020	990
6	7	270	-363
6	8	665	-628
6	9	212	139
6	10	876	-849
6	11	138	173
6	12	0	-86
7	1	719	-702
7	2	89	-133
7	3	549	540
7	4	487	508
7	5	539	534
7	6	780	-769
7	7	150	-231
7	8	374	301
7	9	0	-33
7	10	171	144
7	11	193	263
8	1	102	25
8	2	101	165
8	3	291	263
8	4	268	-245
8	5	629	-646
8	6	402	-446
8	7	384	395
8	8	299	218
8	9	0	-101
8	10	484	441
8	11	246	-117
9	1	1217	1216
9	2	500	516
9	3	92	-18
9	4	173	-208
9	5	660	-654
9	6	610	627
9	7	369	-411
9	8	303	-325
9	9	0	-144
9	10	306	-269
10	1	178	-152
10	2	245	134
10	3	369	-292
10	4	544	604
10	5	601	618
10	6	541	496
10	7	256	-214
10	8	387	-264
10	9	136	118
11	1	312	-297
11	2	209	26
11	3	412	367
11	4	306	298
11	5	324	274
11	6	420	-444
11	7	269	-249
11	8	0	209
12	1	259	127
12	2	203	224
12	3	140	185
12	4	400	-400
12	5	414	-458
12	6	393	-428
13	1	809	781
13	2	254	221
13	3	236	-193
13	4	0	-49

H = 2

K	L	FO	FC
0	0	1491	-1624
0	1	121	-34
0	2	1801	-2001
0	3	653	-670
0	4	1183	1246
0	5	1325	-1388
0	6	842	866
0	7	175	-167
0	8	123	-224
0	9	898	897
0	10	627	641
0	11	533	486
0	12	440	-370
1	0	1479	1645
1	1	801	-808
1	2	0	42
1	3	359	306
1	4	979	-941
1	5	1022	-1014
2	5	454	475
2	6	324	-349
2	7	0	67
2	8	563	538
2	9	144	-179
2	10	530	-457
2	11	170	-111
2	12	128	167
2	13	36	75
3	0	1219	-1220
3	1	1391	1352
3	2	-848	-704
3	3	226	164
3	4	400	411
3	6	494	469
3	7	483	493
3	8	103	114
3	9	1054	-993
3	10	0	41
3	11	178	-113
3	12	0	-49
3	13	244	-61
4	0	621	-622
4	1	64	6
4	2	1439	-1359
4	3	792	-715
4	4	1017	958
4	5	1091	-1029
4	6	962	928
4	7	97	1
4	8	102	-44
4	9	681	603
4	10	500	498
4	11	521	415
4	12	350	-339
4	13	86	-27
5	0	1106	1059
5	1	483	-452
5	2	176	-128
5	3	443	441
5	4	738	-704
5	5	682	-693
5	6	251	116
5	7	331	-334
5	8	0	96
5	9	870	851
5	10	215	-149
5	11	160	-99
5	12	0	-97
6	0	323	299
6	1	480	-456
6	2	832	828
6	3	319	-314
6	4	757	-773
6	5	570	561
6	6	224	-159
6	7	199	187
6	8	583	552
6	9	371	-356
6	10	480	-444
6	11	0	-112
6	12	83	137
7	0	1441	-1385
7	1	676	655
7	2	343	-311
7	3	179	107
7	4	730	721
7	5	913	903
7	6	347	362
7	7	298	345
7	8	19	132
7	9	996	-960
7	10	40	107
7	11	233	-119
8	0	390	-394
8	1	168	127
8	2	810	-804
8	3	337	-331
8	4	701	690
8	5	623	-661
8	6	627	562
8	7	0	-6
8	8	0	-99
8	9	444	395
8	10	284	361
8	11	68	302
9	0	326	317
9	1	448	-446
9	2	146	70
9	3	308	307
9	4	177	-180
9	5	281	-250
9	6	0	65
9	7	301	-312
9	8	247	159
9	9	496	448
9	10	277	-33
10	0	126	25
10	1	243	-186
10	2	508	505
10	3	39	6
10	4	474	-466
10	5	340	366
10	6	281	-288
10	7	200	46
10	8	349	221
10	9	168	-203
11	0	905	-971
11	1	444	370
11	2	200	-181
11	3	0	126
11	4	418	504
11	5	584	609
11	6	335	240
11	7	244	148
11	8	0	146
12	0	248	-345
12	1	103	167
12	2	423	-471

H = 3

K	L	FO	FC
0	3	1581	1430
0	4	360	369
0	5	393	-405
0	6	264	275
0	7	245	-179
0	8	220	-252
0	9	294	-266
0	10	262	-184
0	11	270	262
0	12	0	19
0	13	0	140
1	1	769	-779
1	2	903	875
1	3	491	454
1	4	1580	-1682
1	5	301	291
1	6	249	-213
1	7	203	167
1	8	237	148
1	9	303	212
1	10	758	683
1	11	94	-64
1	12	212	172
1	13	267	-109
2	1	1800	1951
2	2	175	-164
2	3	991	-985
2	4	836	-826
2	5	385	-357
2	6	256	-264
2	7	1025	-1043
2	8	156	311
2	9	18	-94
2	10	352	309
2	11	0	52
2	12	220	200
2	13	156	147
3	1	598	536
3	2	548	-564
3	3	0	98
3	4	1108	1116
3	5	304	-268
3	6	86	-86
3	7	140	-166
3	8	83	109
3	9	0	-28
3	10	450	-431
3	11	0	56
3	12	0	-179
4	1	713	-673
4	2	77	-70
4	3	1104	1103
4	4	352	374
4	5	339	-348
4	6	92	101
4	7	245	186
4	8	199	-204
4	9	147	-180
4	10	0	-128
4	11	0	121
4	12	0	-64
5	1	725	-697
5	2	560	499
5	3	383	360
5	4	1512	-1500
5	5	255	249
5	6	270	-225
5	7	305	204
5	8	302	245
5	9	0	227
5	10	524	709
5	11	0	-76
5	12	0	188
6	1	1732	1751
6	2	120	-125
6	3	894	-896
6	4	492	-564
6	5	235	-232
6	6	366	-329
6	7	543	-468
6	8	230	251
6	9	123	-27
6	10	100	273
6	11	217	-88
7	1	403	374
7	2	943	-946
7	3	331	-292
7	4	802	776
7	5	216	-174
7	6	88	91
7	7	0	-7
7	8	111	62
7	9	63	-82
7	10	311	-310
7	11	209	12
8	1	601	-587
8	2	149	-104
8	3	750	751
8	4	332	326
8	5	0	-109
8	6	0	86
8	7	133	210
8	8	212	-190
8	9	216	-148
8	10	0	-126
9	1	508	-474
9	2	38	-15
9	3	42	-37
9	4	1053	-1085
9	5	292	229
9	6	0	-105
9	7	131	205
9	8	0	128
9	9	290	83
10	1	794	797
10	2	181	-83
10	3	528	-551
10	4	302	-315
10	5	265	-51
12	4	262	223
12	5	190	23
13	1	333	-308
13	2	0	114

H = 4

K	L	FO	FC
0	0	886	888
0	1	141	-139
0	2	522	-499
0	3	704	723
0	4	339	329
0	5	1405	1506
0	6	175	85
0	7	244	224
0	8	468	-466
0	9	1120	-1104
0	10	363	265
0	11	556	-481
0	12	209	-123
1	0	1252	-1275
1	1	720	-724
1	2	357	-318
1	3	728	726
1	4	863	878
1	5	129	87
1	6	404	401
1	7	419	-425
1	8	239	-214
1	9	328	275
1	10	354	276
1	11	323	-291
2	0	1056	-1088
2	1	286	194
2	2	541	565
2	3	347	310
2	4	152	-141
2	5	306	-296
2	6	72	22
2	7	364	-335
2	8	454	492
2	9	453	420
2	10	328	-369
2	11	0	108
2	12	221	66
3	0	1363	1401
3	1	522	529
3	2	701	661
3	3	624	-612
3	4	484	-484
3	5	0	-36
3	6	562	-568
3	7	235	228
3	8	250	-60
3	9	378	-265
3	10	0	-130
3	11	360	307
3	12	216	83
4	0	868	830
4	1	293	244
4	2	536	-534
4	3	767	728
4	4	209	224
4	5	987	966
4	6	0	63
4	7	216	226
4	8	454	-448
4	9	853	-826
4	10	281	278
4	11	308	-460
4	12	224	-128
5	0	755	-755
5	1	593	-556
5	2	118	-119
5	3	649	626
5	4	674	662
5	5	106	53
5	7	403	-398
5	8	345	-312
5	9	252	228
5	10	174	248
5	11	0	-256
6	0	742	-745
6	1	482	469
6	2	335	346
6	3	313	265
6	4	136	-183
6	5	611	-619
6	6	146	17
6	7	305	-227
6	8	361	380
6	9	397	508
6	10	0	-263
6	11	204	61
7	0	1333	1353
7	1	481	505
7	2	414	447
7	3	443	-450
7	4	728	-739
7	5	234	-71
7	6	621	-555
7	7	231	265
7	8	59	-38
7	9	217	-220
7	10	103	-215
8	0	623	616
8	1	27	124
8	2	394	-380
8	3	358	336
8	4	0	131
8	5	629	593
8	6	171	60
8	7	275	225
8	8	341	-310
8	9	415	-595
9	0	303	-355
9	1	293	-282
9	2	126	-104
9	3	381	412
11	0	833	894
11	1	374	303
11	2	421	328
11	3	299	-278
11	4	529	-504
11	5	121	-7
11	6	384	-421
12	0	376	327
12	1	227	-156
12	2	87	-175
12	3	0	31
12	4	202	111

H = 5

K	L	FO	FC
0	1	475	522
0	2	655	-699
0	3	72	-60
0	4	193	-53
0	5	751	-765
0	6	119	172
0	7	785	780
0	8	0	52
0	9	243	-99
0	10	0	35
0	11	233	-235
1	1	377	-347
1	2	306	300
1	3	343	368
1	4	184	66
1	5	233	66
1	6	1047	1078
1	7	171	-128
1	8	586	-619
1	9	158	18
1	10	595	-499
1	11	167	21
2	1	900	-906
2	2	243	135
2	3	353	-386
2	4	392	-421
2	5	1295	1338
2	6	215	-163
2	7	128	75
2	8	192	166
2	9	326	323
2	10	145	120
2	11	186	105
3	1	251	123
3	2	319	-307
3	3	269	-252
3	4	142	114
3	5	0	94
3	6	812	-793
3	7	195	127
3	8	425	412
3	9	136	-26
3	10	252	285
3	11	279	-5
4	1	155	137
4	2	477	-490
4	3	224	176
4	4	0	7
4	5	762	-797
4	6	117	107
4	7	440	450
4	8	82	42
4	9	130	-64
4	10	0	92
4	11	0	-163
5	1	428	-402
5	2	377	394
5	3	376	344
5	4	293	193
5	5	257	120
5	6	973	955
5	7	84	-57
5	8	499	-600
5	9	177	46
5	10	490	-519
6	1	983	-959
6	2	134	245
6	3	143	-82
6	4	172	-269
6	5	929	929
6	6	0	-192
6	7	254	-188
6	8	245	130
6	9	114	289
6	10	42	161
7	1	199	79
7	2	157	57
7	3	234	-237
7	4	256	188
7	5	0	53
7	6	715	-716
7	7	175	206
7	8	253	350
7	9	200	36
8	1	246	183
8	2	351	-319
8	3	184	130
8	4	157	53
8	5	661	-677
8	6	98	71
8	7	323	294
8	8	0	15
9	1	354	-273
9	2	431	429
9	3	261	164
9	4	153	244
9	5	58	83
9	6	594	621
9	7	95	51
10	1	352	-381
10	2	209	147
10	3	0	-131
10	4	0	-145
10	5	587	596

H = 6

K	L	FO	FC
0	5	873	-854
0	6	149	-185
0	7	0	115
0	8	190	-202
0	9	396	378
0	10	71	149
1	0	822	841
1	1	839	-846
1	2	17	50
1	3	177	178
1	4	455	-456
1	5	377	371
1	6	44	-43
1	7	145	-50
1	8	173	-155
1	9	69	30
1	10	0	-60
2	0	695	-710
2	1	0	-225
2	2	519	598
2	3	150	22
2	4	0	42
2	5	317	315
2	6	309	-310
2	7	200	-122
2	8	0	17
2	9	202	-133
2	10	268	-151
3	0	872	-856
3	1	518	534
3	2	274	-229
3	3	365	-384
3	4	248	258
3	5	250	-262
3	6	82	156
3	7	163	92
3	8	279	251
3	9	226	-4
3	10	308	-31
4	0	1226	1242
4	1	132	7
4	2	212	-203
4	3	419	-427
4	4	242	-219
4	5	620	-585
4	6	267	-146
4	7	117	69
4	8	317	-289
4	9	289	275
4	10	0	151
5	0	569	601
5	1	824	-812
5	2	26	-33
5	3	0	17
5	4	337	-368
5	5	0	255
5	6	81	44
5	7	226	-38
5	8	0	-81
5	9	0	88
6	0	760	-730
6	1	337	-303
6	2	381	398
6	3	216	36
6	4	141	144
6	5	437	476
6	6	227	-224
6	7	162	-127
6	8	0	-100
6	9	186	-170
7	0	816	-790
7	1	472	474
7	2	167	-154
7	3	271	-333
7	4	364	373
7	5	363	-393
7	6	213	156
7	7	0	43
7	8	0	195
8	0	859	856
8	1	219	61
8	2	217	-193
8	3	242	-228
8	4	282	-152
8	5	446	-415
8	7	0	45
9	0	481	349
9	1	485	-491
9	2	89	6
9	3	181	-40
9	4	97	-144
9	5	0	22
9	6	0	54
10	0	489	-489
10	1	0	-74
10	2	277	244
10	3	0	93
10	4	0	84
11	0	488	-535

H = 7

K	L	FO	FC
0	1	350	-392
0	2	475	454
0	3	418	416
0	4	263	208
0	5	183	-256
0	6	452	-399
0	7	283	273
0	8	233	18
0	9	248	-79
1	1	452	427
1	2	221	179
1	3	203	-157
1	4	645	-648
1	5	357	-418
1	6	175	209
1	7	76	102
1	8	140	-19
3	5	194	252
3	6	318	-227
3	7	0	-123
3	8	193	106
3	9	241	-114
4	1	292	-279
4	2	231	271
4	3	344	353
4	4	184	149
4	5	140	-186
4	6	226	-258
4	7	358	319
4	8	241	-17
5	1	508	490
5	2	0	136
5	3	173	-135
5	4	571	-587
5	5	415	-437
5	6	130	176
5	7	0	0
5	8	139	-12
6	1	479	406
6	4	329	250
6	5	145	185
6	6	520	460
6	7	435	-287
7	1	0	-116
7	2	176	-162
7	3	0	153
7	4	405	415
7	5	211	181
7	6	227	-166
8	1	206	-241
8	2	255	163
8	3	245	298
8	4	122	69
8	5	0	-130
9	1	333	372
9	2	227	27
9	3	0	50

H = 8

K	L	FO	FC
0	0	493	-498
0	1	155	189
0	2	535	-540
0	3	192	84
0	4	533	531
0	5	134	-44
0	6	273	254
0	7	0	110
1	0	0	42
1	1	246	-158
1	2	193	-117
1	3	160	251
1	4	88	-25
1	5	290	-365
1	6	195	178
1	7	147	-203
2	0	274	-214
2	1	151	-208
2	2	211	207
2	3	78	-163
2	4	302	-314
2	5	0	71
2	6	221	34
2	7	0	-24
3	0	117	-83
3	1	290	306
3	2	129	163
3	3	100	-74
3	4	134	61
3	5	372	320
3	6	182	-193
3	7	156	175
4	0	253	-283
4	1	223	156
4	2	470	-458
4	3	0	59
4	4	386	394
4	5	0	-55
4	6	295	272
5	0	190	21
5	1	43	-83
5	2	242	-104
5	3	341	320
5	4	57	-19
5	5	295	-246
5	6	0	175
6	0	0	23
6	1	190	-157
6	2	186	156
6	3	272	-152
6	4	350	-352
6	5	192	18
7	0	220	-66
7	1	197	175
7	2	205	73
7	3	0	-23
8	0	0	-155

H = 9

K	L	FO	FC
0	1	0	-38
0	2	338	-357
0	3	345	314
0	4	309	159
0	5	246	-263
1	1	321	-320
1	2	306	284
1	3	313	251
1	4	308	-211
1	5	99	80
2	1	237	220
2	2	193	-4

(Continued overleaf)

TABLE III. (Continued)

2	12	49	-237	1	6	104	-94	12	3	0	-11	10	6	68	-139	9	4	134	208	10	6	224	-115	1	9	0	55	2	3	249	-255
2	13	254	-308	1	7	455	-441	12	4	406	421	10	7	357	-362	9	5	145	28	11	1	171	47	2	1	457	447	2	4	412	-387
3	1	1500	-1350	1	8	0	9	12	5	402	-425	10	8	48	125	9	6	0	-1	11	2	223	100	2	2	203	208	2	5	244	112
3	3	0	38	1	9	1161	1105	12	6	205	163	11	1	230	197	9	7	252	-176	11	3	338	-221	2	3	374	-348	3	1	213	212
3	4	893	847	1	10	295	-155	13	0	264	251	11	2	679	-687	9	8	310	-246	11	4	190	205	2	5	243	163	3	2	326	-300
3	5	474	457	1	11	98	-22	13	1	250	-117	11	3	275	-231	10	0	473	-471					2	6	429	431	3	3	141	-172
3	6	929	-966	1	12	0	-47	13	3	323	282	11	4	285	381	10	1	0	100		H =	6		2	7	405	-429	3	4	93	167
3	7	123	116	1	13	0	15	13	4	238	-249	11	5	103	-49	10	2	246	264					2	8	276	-192	4	1	264	-23
3	8	320	361	2	0	448	-467					11	6	174	23	10	3	0	-25	0	0	1458	1566	2	9	0	-18	4	2	294	-219
3	9	0	19	2	1	-736	-638		H =	3		11	7	0	16	10	4	0	-103	0	1	207	186	3	1	0	-177	4	3	352	253
3	10	259	239	2	2	814	823					12	1	621	-635	10	5	409	-345	0	2	0	-150	3	2	135	-91	5	1	315	-333
3	11	95	86	2	3	294	-295	0	1	1279	-1274	12	2	205	-21	10	6	0	18	0	3	441	-468	3	3	157	-37	5	2	215	217
3	12	63	-139	2	4	887	-886	0	2	148	-90	12	3	524	499	10	7	0	-131	0	4	337	-352	3	4	545	519				

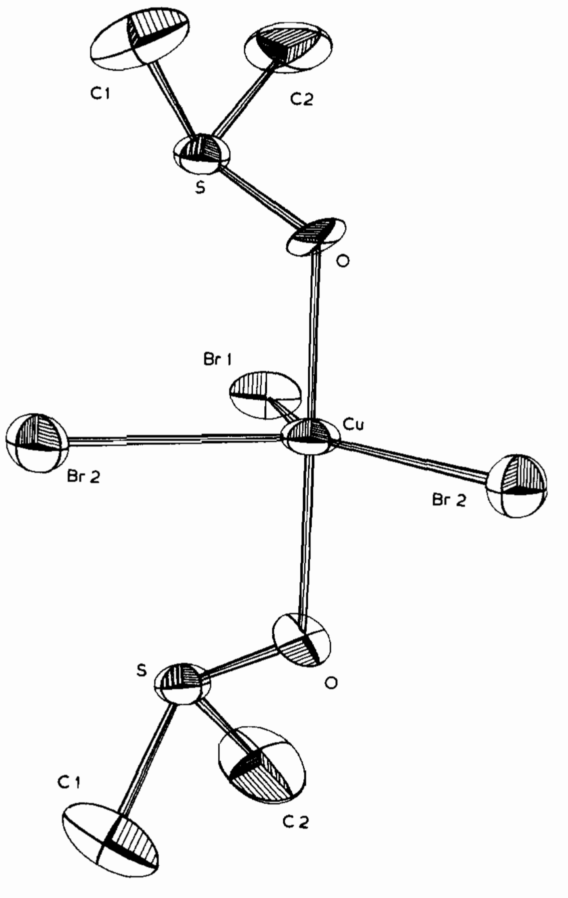

Fig. 1. Coordination sphere of copper(II) in $CuBr_2 \cdot 2DMSO$.

consider the coordination geometry as distorted square pyramidal than distorted trigonal bipyramidal. Examination of bond distances in the bromide analog would indicate it is again more appropriate to describe the geometry as distorted square pyramidal. The two shorter Cu–Br distances (2.43, 2.45Å) are comparable to the equatorial distances for the distorted octahedral geometry in $CsCuBr_3$ (2.45Å average) [2]. The equatorial Cu–Br distances for the trigonal bipyramidal geometry (2.52Å) are distinctly longer [4, 5]. Thus, we envisage the structure as derived from the severe distortion of a planar four-coordinate species (two bromine, two oxygen ligands) by the presence of a fifth axial ligand.

It is instructive to make a detailed comparison of the interatomic distances in the copper chromophores of the two DMSO complexes. The axial Cu–Br distance is 2.777(4)Å, approximately 0.34Å longer than the other two Cu–Br distances. The opposite bond angle is 146.13(2)°. In the chloride salt, the axial Cu–Cl bond is 0.42Å longer than equatorial bonds while the bond angle is identical. Thus the axial bond only elongated 0.08Å. The change in the short bond Cu–X bond lengths between the chloride and bromide salt is roughly 0.15Å, corresponding precisely to the change in ionic radii of the two halide ions. Thus the only steric compression in the chromophore upon change from bromide to chloride is in the axial Cu–X distance. This is born out by examination of the non-bonded interactions in the coordination sphere. The only short contacts are the X–O inter-

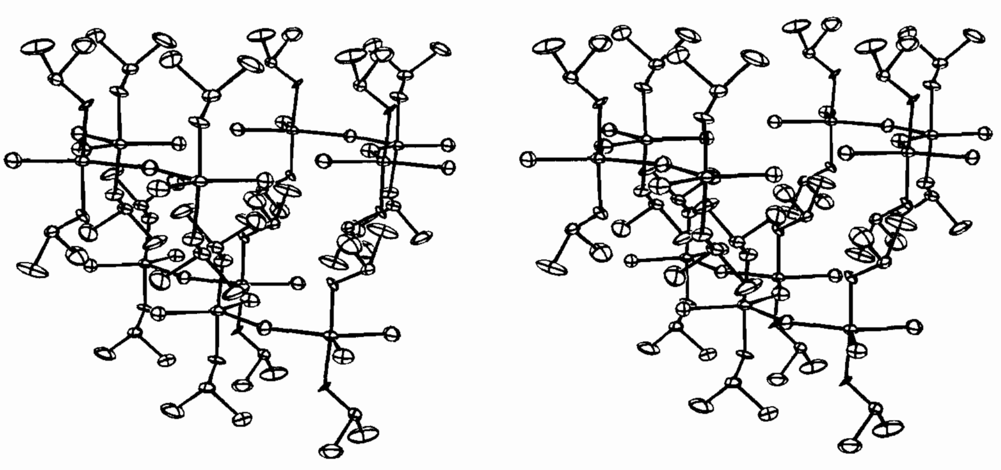

Fig. 2. Stereographic view of the crystal structure of $CuBr_2 \cdot 2DMSO$ as viewed from near the b-axis.

actions since the X–X interactions are all greater than the sum of the van der Waals radii. The X_1–O and X_2–O distances are less than the sum of the van der Waals radii since both ligands are strongly bonded to the copper. In the chloride salt, the Cl'_1–O distance is exactly equal to this sum, as pointed out previously. However, in the bromide salt, the Br'_1–O distance is 0.1Å shorter than the sum.

The source of this steric compression logically lies in crystal packing forces, implying that the coordination geometry is largely determined by *inter*molecular steric forces, rather than *intra*molecular forces. Indeed, examination of the packing of the chains clearly shows that the methyl groups and halides neatly interlock, fixing their locations. The copper geometry thus largely reflects these steric interactions, rather than the inherent stability of the observed geometry of the chromophore.

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