might be due to packing considerations and one might assume that one chlorine atom is bent 32° from the plane because of an interaction with the pyridine ring. A consideration of contact distances does not show the chlorine atom to be significantly closer when it is placed in the copper–oxygen plane than when it is bent out of the plane. We do not believe that a steric interaction would be sufficiently strong to give the resulting distorted structure. Some careful theoretical considerations will have to be employed to see if the proposed mechanism is possible.

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The Crystal Structure of Tris(2-dimethylaminoethyl)aminecobalt(II) Bromide

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The crystal structure of Co(Me$_6$tren)Br$_2$ [Me$_6$tren = N(CH$_2$CH$_2$N(CH$_3$)$_2$)$_3$] has been determined by three-dimensional X-ray analysis and refined to a final R factor of 8.0%. Crystals of the compound are cubic, space group P2$_1$3, $a = 12.088 \pm 0.004$ A, with four formula units per unit cell. The structure consists of Co(Me$_6$tren)Br$^+$ and Br$^-$ ons arranged in a distorted NaCl lattice. The Co(Me$_6$tren)Br$^+$ ion has a trigonal bipyramidal structure with symmetry C$_3$. The symmetry of the complex ion is essentially determined by the shape of the ligand molecule. The series of complexes M^{II}(Me$_6$tren)Br$_2$ with M^{II} = Cr, Mn, Fe, Co, Ni, Cu, and Zn are all isomorphous.

Introduction

Although several five-coordinated cobalt(II) complexes have been described by X-ray analysis,[1-6] the factors determining the stereochemistry of these complexes are not well understood. From the results it appears that, among the other factors, the geometry of the ligand molecule plays an important role in determining the stereochemistry of the complex.

Ciampolini and Nardi[7] have reported the preparation and the physicochemical properties of a series of high-spin complex compounds with general formula M^{II}(Me$_6$tren)X$_2$, where M^{II} = Cr, Mn, Fe, Co, Ni, Cu, and Zn and Me$_6$tren = tris(2-dimethylaminoethyl)amine, N(CH$_2$CH$_2$N(CH$_3$)$_2$)$_3$, and X = Cl, Br, I, NO$_3$, and ClO$_4$.

On the basis of magnetic, spectral, and conductivity measurements, these complexes have been formulated as [M(Me$_6$tren)X]X, and a trigonal bipyramidal structure has been proposed for the [M(Me$_6$tren)X]$^+$ ion.

All the complexes with the same anion are isomorphous, as shown by the similarity of their X-ray powder patterns. The bromides crystallize in well-formed tetrahedra with dimensions particularly suitable for X-ray investigation. We report here the three-dimensional X-ray analysis of the complex [Co(Me$_6$tren)Br]Br.

Experimental Section

Data Collection.—Crystals of the complex suitable for the structural analysis were kindly supplied by Dr. Ciampolini. Cell dimensions were determined from a Weissenberg photograph using Fe Kα radiation (λ 1.9373 A), with the NaCl rotation pattern superimposed on the film for calibration ($a = 5.6273$ A). Six 2θ values were measured and treated by least squares. The results are: $a = 12.088 \pm 0.004$ A, $d_o = 1.688$ g/cm^3, $Z = 4$, $\mu = 139.0$ cm^{-1}, space group P2$_1$3.

The crystal chosen for the collection of the intensities was a truncated tetrahedron with the edge of about 0.25 mm.

Doubly integrated Weissenberg photographs *hk*0 through *hk*6 were taken on a Nonius camera, with the multiple-film, equi-inclination technique. The intensities of the reflections were measured on a Nonius microdensitometer, the intensity being assumed proportional to the density of the spots. The various levels were scaled by means of common reflections. We examined 390 independent reflections, about 95% of the total number in the Fe sphere of reflection; we found 53 too weak to be measured.

Intensities were corrected for Lorentz and polarization effects and for spot elongation on upper levels according to Phillips.[8]

Later, during the determination of the structure, inspection of the observed and calculated structure factors at $R = 12.1\%$ showed the existence of strong secondary extinction effects. This was confirmed by a plot of ln (I_c/I_o) against I_c for the strongest reflections, but an attempt to correct all of the reflections on the basis of the plot did not give satisfactory results. It was decided then to continue the refinement, omitting those reflections which appeared to be affected most heavily by extinction. These reflections are 210, 220, 121, 231, 331, 431, 241, 351, 171, 222, and 262.

The atomic scattering factors were taken from the Dirac–

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Table I

Positional Parameters, Temperature Factors, and Their Estimated Standard Deviations[a]

	Positional parameter × 10^4			Thermal parameter × 10^4					
Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2280 (3)	2280 (3)	2280 (3)	44 (2)	44 (2)	44 (2)	−1 (2)	−1 (2)	−1 (2)
Br(1)	1119 (2)	1119 (2)	1119 (2)	52 (2)	52 (2)	52 (2)	−8 (2)	−8 (2)	−8 (2)
Br(2)	8151 (2)	8151 (2)	8151 (2)	61 (2)	61 (2)	61 (2)	5 (2)	5 (2)	5 (2)
N(1)	3308 (17)	3308 (17)	3308 (17)	60 (16)	60 (16)	60 (16)	10 (15)	10 (15)	10 (15)
N(2)	2752 (16)	1106 (16)	3446 (15)	32 (15)	54 (15)	41 (15)	6 (13)	−4 (13)	−25 (13)
C(1)	3619 (18)	2698 (19)	4292 (18)	49 (16)	64 (17)	8 (17)	2 (15)	−7 (14)	30 (15)
C(2)	3820 (18)	1470 (17)	3993 (18)	21 (15)	46 (16)	47 (16)	23 (14)	−18 (15)	−3 (13)
C(3)	2957 (22)	−54 (23)	2984 (22)	55 (23)	53 (22)	92 (21)	39 (19)	21 (20)	−16 (18)
C(4)	1868 (27)	945 (26)	4294 (25)	103 (25)	62 (25)	77 (24)	−24 (23)	−13 (22)	23 (21)

[a] Anisotropic thermal factors are of the form: $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_ih_j\beta_{ij})$. Estimated standard deviations are given in parentheses.

Slater calculations of Cromer and Waber.[9] No correction was made for anomalous dispersion or for absorption effects.

Structure Determination.—The positions of the heavy atoms were determined by means of a three-dimensional Patterson synthesis. There are eight bromine and four cobalt atoms in the unit cell. Examination of the equivalent positions of the space group $P2_13$ shows that these atoms must lie on the threefold axes, *i.e.*, in 4a: x, x, x; $1/2 + x, 1/2 - x, \bar{x}$; $\bar{x}, 1/2 + x, 1/2 - x$; $1/2 - x, \bar{x}, 1/2 + x$. Each set of equivalent atoms generates a set of 12 peaks in the vector space lying in the three Harker sections having, respectively, $u = 1/2$, $v = 1/2$, $w = 1/2$. On the other hand, two different sets of equivalent atoms in 4a give rise to 32 vectors, eight of which lie along the threefold axes. One of the bromine atoms was located from one of the two Harker sets which showed the highest peaks. The second bromine atom and the cobalt atom were successively located from the peaks lying along the threefold axes. These positions were then checked for all of the highest peaks in the Patterson synthesis.

The Fourier synthesis phased on the positons of the heavy atoms showed clearly all the other nonhydrogen atoms. At this point the R factor was 13.6%, but some of the bond lengths between light atoms were rather improbable. R is throughout defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, where the sums are over the independent, observed reflections.

A ΔF synthesis calculated at this point did not give any decisive improvement. Refinement was then continued by means of block-diagonal, least-squares analysis, with individual isotropic temperature factors for the atoms. Reflections were weighted according to the function:[10] $w = 1/(a + F_o + cF_o^2)$, with $a = 30.0$ and $c = 0.02$ A. Unobserved reflections were not introduced in this series of calculations. A set of three cycles reduced the R factor to 12.1% but the C–C bond length still appeared to be rather long (1.69 A).

It was then decided to continue the refinement with the full-matrix, least-squares program of Busing and Levy, adapted for the 7090 by Stewart.[11]

Unobserved reflections were introduced in this set of calculations with the minimum observable intensity. Reflections affected by extinction were omitted as mentioned above. The weighting scheme used was as follows: $\sqrt{w} = 0$ for unobserved reflections with $F_c \leqslant F_{min}$; $\sqrt{w} = 1$ for unobserved reflections with $F_c > F_{min}$ and for observed reflections with $F_o \leqslant 60$; $\sqrt{w} = 60/F_o$ for observed reflections with $F_o > 60$.

Three cycles with individual isotropic temperature factors reduced the R factor to 9.1%. The C–C bond length showed a decisive improvement (1.59 A).

At this point the hydrogen atoms were introduced in calculated positions with a thermal parameter $B = 4.0$ A^2, and their coordinates were not refined. Individual anisotropic temperature factors were applied to all the nonhydrogen atoms. One more cycle of least squares gave a final R factor of 8.0% and for the C–C bond a satisfactory value of 1.55 A. It should be noted that in this cycle the temperature factor of C(1) went nonpositive definite, probably owing to the uncorrected absorption.

Table I reports the final atomic parameters and the temperature factors with their estimated standard deviations. Standard deviations of the parameters were calculated from the expression

$$\sigma_i = \sqrt{\frac{(\Sigma w\Delta^2)a_{ii}}{n - s}}$$

where a_{ii} is the diagonal term of the inverse least-squares matrix, n is the number of observations, and s the number of parameters. Table II reports the coordinates of the hydrogen atoms and Table III the observed and calculated structure factors.

Table II

Coordinates of Hydrogen Atoms

Atom	$10^4x/a$	$10^4y/b$	$10^4z/c$
H′(1)	4343	3066	4646
H″(1)	2951	2760	4889
H′(2)	4515	1382	3431
H″(2)	3989	0973	4715
H′(3)	2197	−0290	2584
H″(3)	3612	−0030	2380
H‴(3)	3160	−0609	3625
H′(4)	1088	0685	3926
H″(4)	2104	0293	4875
H‴(4)	1716	1682	4761

All of the calculations, with the exception of the full-matrix, least-squares cycles, were performed with a set of programs written for the IBM 1620 by Albano, Bellon, Pompa, and Scatturin.[12]

Discussion

The structure of $Co(Me_6tren)Br_2$ consists of $Co(Me_6tren)Br^+$ and Br^- ions arranged in a distorted NaCl lattice. Each cation is surrounded by three Br^- ions at 5.65 A and three at 6.67 A, forming a distorted octahedron.

The $Co(Me_6tren)Br^+$ ion (Figure 1) has a trigonal bipyramidal structure with symmetry C_3. The cobalt atom is five-coordinated by the four nitrogen atoms of the amine and by one bromine atom. Bond lengths and angles in the ion with their estimated standard deviations are reported in Table IV.

The average Co–N distance of 2.11 A is in good agree-

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TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H,1,0			
2	799E	981	0
3	268	264	750
4	925	1092	999
5	193L	89	249
6	293	297	999
7	728	758	249
8	713	670	0
9	277	200	249
10	262	239	0
11	463	401	249
12	356	310	0
H,2,0			
1	333	389	249
2	873E	1033	0
3	176	146	249
4	536	545	0
5	874	986	249
6	347	331	0
7	252L	42	750
8	269L	213	999
9	646	610	249
10	252L	13	999
11	223	205	749
12	141	113	0
H,3,0			
1	757	810	750
2	850	1037	0
3	464	434	750
4	688	697	0
5	753	747	749
6	1217	1354	999
7	1111	1180	249
8	323	304	999
9	516	541	249
10	244L	26	999
11	209	179	749
H,4,0			
0	922	901	0
1	631	686	750
2	718	894	0
3	503	517	749
4	1417	1607	999
5	234	236	249
6	343	317	999
7	266L	59	249
8	277	248	999
9	261L	66	249
10	395	406	999
11	461	455	249
H,5,0			
1	1004	1071	249
2	311	340	999
3	523	543	749
4	234	200	999
5	957	1077	249
6	431	419	0
7	276	235	749
8	273	299	939
9	364	303	249
10	214	211	0
11	418	393	749
H,6,0			
0	236	224	0
1	686	716	249
2	228L	124	999
3	238L	155	750
4	250L	109	0
5	643	618	750
6	696	677	0
7	271L	179	749
8	768	766	0
9	226L	21	249
10	181L	171	999
H,7,0			
1	247L	92	750
2	310	286	999
3	340	296	249
4	558	571	999
5	522	485	749
6	552	524	0
7	265	186	249
8	404	348	0
9	198L	109	749
10	434	468	999
H,8,0			
0	270	216	999
1	525	512	249
2	316	272	999
3	606	646	750
4	377	355	0
5	269L	105	750
6	698	704	999
7	236L	78	249
8	600	651	0
9	434	474	749
H,9,0			
1	1076	1107	249
2	368	371	999
3	269L	165	749
4	320	308	999
5	249L	84	249
6	228L	25	999
7	366	367	749
8	166	190	999
H,10,0			
0	664	648	999
1	564	599	249
2	252L	177	0
3	567	633	749
4	253	233	999
5	210L	2	751
6	164	173	999
7	258	222	749
H,11,0			
1	453	503	749
2	373	379	999
3	473	462	249
4	178L	2	998
5	147L	73	749
H,12,0			
0	158	127	0
1	151L	40	249
2	141	124	0
H,2,1			
1	643E	844	917
2	872	1023	72
3	799	874	123
4	329	284	821
5	532	459	894
6	244	171	810
7	542	506	159
8	271L	39	877
9	648	669	757
10	378	371	51
11	528	555	808
12	223	229	91
H,3,1			
1	692	792	106
2	1077E	1426	66
3	1107E	1421	838
4	1070E	1268	106
5	532	555	237
6	582	557	951
7	261L	86	764
8	321	303	822
9	414	409	870
10	366	384	848
11	296	322	191
H,4,1			
1	343	353	866
2	1029E	1251	82
3	360	301	835
4	551	539	914
5	812	818	242
6	462	455	214
7	692	671	843
8	597	555	921
9	308	230	978
10	253	251	829
11	292	261	193
H,5,1			
1	683	775	146
2	278	285	171
3	819E	996	757
4	1041	1135	13
5	908	945	965
6	839	909	956
7	341	334	123
8	274	211	140
9	371	384	16
10	213	198	944
11	147	138	98
H,6,1			
1	561	602	737
2	683	749	914
3	871	1016	164
4	527	537	984
5	564	532	173
6	273L	39	925
7	499	490	876
8	507	503	58
9	228L	105	863
10	180L	111	866
H,7,1			
1	1003E	1334	230
2	287	271	20
3	261L	152	780
4	759	788	824
5	375	335	61
6	425	404	28
7	261L	89	231
8	296	253	103
9	231	228	873
10	337	406	879
H,8,1			
1	395	379	198
2	682	707	830
3	705	720	808
4	274L	206	900
5	307	324	782
6	301	451	28
7	393	360	71
8	288	275	898
9	157	144	72
H,9,1			
1	558	615	852
2	414	411	70
3	285	252	947
4	373	304	962
5	344	317	966
6	284	318	36
7	208	173	756
8	376	415	960
H,10,1			
1	257L	101	200
2	256	180	33
3	268	276	909
4	270	274	868
5	377	375	240
6	486	510	932
7	321	360	103
H,11,1			
1	216L	40	892
2	209L	114	953
3	224	270	185
4	326	336	832
H,12,1			
1	232	207	36
2	143	123	168
H,2,2			
2	1004E	1103	126
H,3,2			
2	939	994	111
3	473	425	751
4	743	800	69
5	891	971	89
6	747	710	879
7	437	406	192
8	617	640	855
9	629	625	886
10	242	269	996
11	174L	79	788
H,4,2			
2	962	1014	856
3	991	1074	61
4	712	680	888
5	430	435	157
6	269	201	957
7	580	549	49
8	339	296	76
9	305	282	832
10	219	225	765
11	444	509	892
H,5,2			
2	320	292	177
3	541	496	960
4	858	831	752
5	421	388	239
6	309	299	875
7	584	542	207
8	328	297	23
9	277	241	214
10	367	396	864
11	169	193	964
H,6,2			
2	1011E	1161	755
3	527	539	967
4	466	455	998
5	246L	126	821
6	681	631	100
7	603	593	952
8	468	478	858
9	394	405	818
10	160	216	856
H,7,2			
2	464	442	37
3	290	279	915
4	388	364	149
5	869	822	949
6	250L	125	770
7	345	303	732
8	216	176	812
9	541	637	39
10	186	236	945
H,8,2			
2	566	506	754
3	490	434	38
4	334	325	61
5	247L	178	807
6	418	423	938
7	640	679	949
8	182	143	76
9	243	259	871
H,9,2			
2	264	210	999
3	549	513	880
4	495	469	797
5	265	296	907
6	208	177	123
7	174L	94	998
8	231	233	782
H,10,2			
2	641	693	765
3	477	436	894
4	285	220	792
5	347	374	834
6	160	180	992
7	240	341	156
H,11,2			
2	282	274	803
3	384	399	810
4	218	214	139
5	174	229	29
H,12,2			
2	110L	118	826
H,3,3			
3	719	818	958
H,4,3			
3	709	794	153
4	266	248	776
5	337	273	108
6	358	354	241
7	583	593	981
8	293L	16	186
9	563	613	875
10	231L	76	932
11	179	188	758
H,5,3			
3	378	369	888
4	263L	93	82
5	797	905	960
6	297	230	755
7	409	359	853
8	547	556	937
9	290	306	993
10	242	260	999
H,6,3			
3	673	752	32
4	474	487	122
5	667	667	204
6	424	412	908
7	498	500	878
8	400	379	888
9	242	195	46
10	170	164	15
H,7,3			
3	725	795	772
4	420	410	812
5	545	565	835
6	329	326	876
7	407	399	771
8	365	378	928
9	193	190	853
H,8,3			
3	296L	91	223
4	553	533	885
5	544	526	221
6	283	258	846
7	281	260	53
8	196L	109	817
H,9,3			
3	288	232	856
4	277	221	97
5	259	259	66
6	483	538	928
7	190L	124	182
H,10,3			
3	417	433	795
4	379	379	919
5	259	269	919
6	170	159	797
H,11,3			
3	357	394	854
4	204	240	224
H,4,4			
4	896	864	218
H,5,4			
4	217	175	981
5	378	339	9
6	556	566	802
7	584	500	231
8	702	723	805
9	381	395	36
10	190	190	900
H,6,4			
4	634	664	898
5	485	439	142
6	301	300	763
7	403	385	904
8	227	206	907
9	464	544	786
10	255	267	201
H,7,4			
4	532	487	878
5	243	215	827
6	580	622	963
7	311	307	216
8	177	173	201
9	158	218	90
H,8,4			
4	564	614	67
5	567	510	826
6	269	244	776
7	373	385	871
8	233	243	944
H,9,4			
4	330	326	820
5	307	279	862
6	165L	102	808
7	217	183	163
H,10,4			
4	485	505	847
5	375	418	779
6	280	363	176
H,5,5			
5	312	196	798
H,6,5			
5	353	298	867
6	613	542	888
7	361	347	164
8	263	193	5
9	196	178	788
H,7,5			
5	342	264	845
6	453	489	751
7	258	193	27
8	401	519	796
H,8,5			
5	311	305	968
6	534	630	776
7	208L	189	941
H,9,5			
5	349	391	952
6	318	394	904
H,10,5			
5	203	268	922
H,6,6			
6	429	433	111
H,7,6			
6	222L	148	969
7	191L	39	795
8	231	257	924
H,8,6			
6	465	430	806
7	138L	37	65

[a] Columns are l index, $10F_o$, $10F_c$, and α (millicycles). Unobserved reflections are marked by L; reflections considered affected by extinction are marked by E.

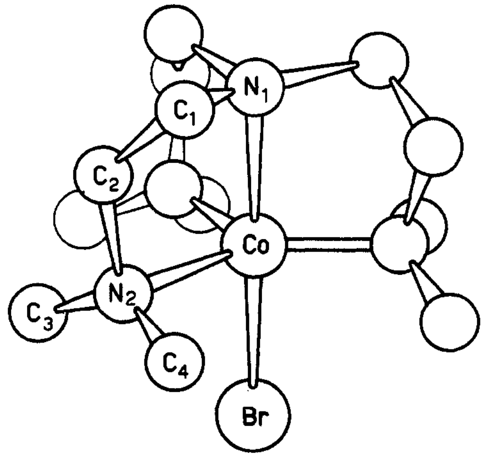

Figure 1.—A perspective drawing of the Co(Me$_6$tren)Br$^+$ ion.

TABLE IV

DISTANCES AND ANGLES IN THE Co(Me$_6$tren)Br$^+$ ION WITH THEIR ESTIMATED STANDARD DEVIATIONS[a]

Distance, A			Angle, deg		
Co–N(1)	2.151	0.021	N(1)–Co–N(2)	81.1	0.8
Co–N(2)	2.080	0.018	N(2)–Co–Br(1)	98.9	0.5
Co–Br(1)	2.431	0.004	N(2)–Co–N(2′)	117.6	0.7
N(1)–C(1)	1.449	0.029	Co–N(1)–C(1)	109.3	1.4
C(1)–C(2)	1.547	0.031	N(1)–C(1)–C(2)	109.7	1.8
C(2)–N(2)	1.515	0.028	C(1)–C(2)–N(2)	104.3	1.7
N(2)–C(3)	1.529	0.033	C(2)–N(2)–C(3)	106.7	1.7
N(2)–C(4)	1.492	0.036	C(2)–N(2)–C(4)	110.4	1.8
Br(1)–C(3)	3.468	0.026	C(3)–N(2)–C(4)	104.3	1.9
Br(1)–C(4)	3.950	0.030	Co–N(2)–C(3)	115.0	1.4
Br(1)–N(2)	3.437	0.018	Co–N(2)–C(4)	111.0	1.6
N(2)–N(2′)	3.558	0.026	Co–N(2)–C(2)	109.3	1.3

[a] Primes refer to atoms related to reference atom by the threefold axis.

ment with the analogous 2.12 A reported for (1,3-bis-(2′-pyridyl)-2,3-diaza-1-propene)cobalt(II) chloride[4] and with the 2.13 A of Co(Me$_5$dien)Cl$_2$[3] [Me$_5$dien = (CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)$_2$]. It should be noted that the axial Co–N distance is about three standard deviations longer than the equatorial Co–N distances, but the difference is hardly significant since standard errors in Table IV are probably underestimates. The comparison with the structures of the isomorphous complexes of the series, in progress in our laboratory, will further elucidate this question.

The Co–Br distance of 2.43 A is in good agreement with the sum (2.43 A) of the Pauling covalent radii of the cobalt (octahedral) and of the bromine. Since the bond cannot be purely covalent, owing to the different electronegativity of the two elements, this seems to indicate the existence of π bonding between the metal and the halogen atom, which would contribute to the stability of the complex.

The N(1)–Co–N(2) angle of 81.1° appears essentially imposed by the stereochemistry of the ligand molecule, although this value is somewhat smaller than those found in ethylenediamine metal chelates.[13] This causes the metal atom to lie 0.32 A below the equatorial plane of the three nitrogen atoms. The angles formed by the equatorial nitrogen atoms at the cobalt are 117.6°. Bond lengths and angles in the ligand molecule appear to be normal (Table IV).

Gillespie[14] has discussed the main factors which determine the configuration of five-coordinate complexes. Although the electrostatic repulsions between the ligands favor the trigonal bipyramidal configuration, crystal field stabilization energy favors the square-pyramidal configuration, and this effect should predominate in complexes with essentially ionic binding. Anyhow, in most cases, both effects will be comparable and the resultant structure will be intermediate between the two configurations, or other factors, such as the shape of the ligand molecule or packing effects in the solid state, may determine the structure of the complex.

Of the reported structures of five-coordinated cobalt(II) complexes, three[1,2,4] have been described as more or less distorted square pyramids, and three[3,5,6] are intermediate between the two configurations. Co(Me$_6$tren)Br$_2$ is then the first five-coordinate cobalt(II) complex having a trigonal bipyramidal structure with C_3 symmetry. Undoubtedly the symmetry of the complex cation is determined by the particular shape of the ligand molecule.

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(13) J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, **5**, 1770 (1966), and references therein.

(14) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).