such studies will provide further useful data on metal–nitrogen multiple bonds.

Thermal Motions of the Atoms

The principal root-mean-square amplitudes of vibration for the atoms that were refined anisotropically are listed in Table IX. The directions of vibration can be seen in Figure 1. With the possible exception of the O atom and CH_3 group of the methoxy structure the values appear to be physically reasonable. (The O atom and CH_3 group are suspect because they lie very close to the C_2 axis in the disordered model.)

It is possible to apply "corrections" to the bond lengths assuming various vibration models.[28] The most reasonable model in this case would be one in which the atoms bonded to the Re atom ride on the Re atom. An alternative model allows the atoms to vibrate independently. The bond lengths after correction with these two models are shown in Table X.

It is important to keep in mind that generally the errors of assumption in the thermal model exceed the precision with which the bond lengths have been determined. The point we wish to make here is that the difference between the Re–N distances in the methoxy and acetyl compounds is not substantially affected by choice of thermal model.

TABLE X

BOND LENGTHS (Å) AFTER CORRECTION FOR THERMAL VIBRATION (a) ASSUMING RIDING MODEL AND (b) ASSUMING INDEPENDENT MOTION

	Methoxy			Acetyl		
Bond	Uncor	a	b	Uncor	a	b
Re–N	1.709	1.711	1.752	1.690	1.690	1.735
Re–Cl_1	2.432	2.444	2.473	2.410	2.420	2.451
Re–Cl_2	2.421	2.432	2.455	2.399	2.409	2.438
Re–Cl_3				2.433	2.443	2.472
Re–P_1	2.470	2.473	2.497	2.457	2.459	2.487
Re–P_2				2.461	2.466	2.494

Acknowledgments.—We are indebted to Professor J. Chatt and Miss J. Paske for the various samples and for useful discussions. We have also enjoyed very interesting discussions on the nature of the bonding in these compounds with Professors L. F. Dahl, B. Lever, and R. G. Pearson. We are grateful to the National Institutes of Health and the National Science Foundation for their support of this work.

---

[28] W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

The Structure of Hexaamminechromium(III) Pentachlorocuprate(II), $[Cr(NH_3)_6][CuCl_5]$

BY KENNETH N. RAYMOND, DEVON W. MEEK, AND JAMES A. IBERS

Received January 22, 1968

The crystal structure of hexaamminechromium(III) pentachlorocuprate(II), $[Cr(NH_3)_6][CuCl_5]$, has been redetermined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group Fd3c of the cubic system with 32 formula units in a cell 22.240 (7) Å on an edge. The calculated density of 1.908 g/cm^3 agrees well with that of 1.892 g/cm^3 measured previously. The structure has been refined by least-squares methods to a final R factor on F of 3.7% for the 633 reflections above background. The positions of the hydrogen atoms of the ammine groups were included in this refinement. In addition, the charges on the atoms were determined. The $Cr(NH_3)_6^{3+}$ ion is required crystallographically to have $\bar{3}$ site symmetry. The coordination geometry is octahedral. The N–Cr–N angle is 89.65 (12)° and the Cr–N bond length is 2.0644 (25) Å. The $[CuCl_5]^{3-}$ ion is required crystallographically to have 32 site symmetry and is therefore a regular trigonal bipyramid. There are two independent Cu–Cl distances, one along the threefold axis and one in the equatorial plane. The Cu–Cl bond lengths, uncorrected for the effects of thermal motion, are $Cu–Cl_{ax} = 2.2964$ (12), $Cu–Cl_{eq} = 2.3912$ (13) Å. This significant shortening of the axial bond lengths in a trigonal-bipyramidal MX_5 complex is compared with results available for other MX_5 complexes. This shortening may be explained by the stereochemical activity of the 3d electrons.

Introduction

The number of authentic five-coordinate transition metal complexes has increased dramatically during the past 4 years.[1] In trying to formulate a systematic basis for those factors which favor a given five-coordinate structure, one discovers that most examples are complicated by the utilization of polydentate ligands,[2] some of which impose their own stereochemistry on the resulting complexes.[2c,3] That electronic and π-bonding considerations may be important factors in stabilizing five-coordination has become apparent recently from

---

[1] For example, see the relatively recent reviews: (a) J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 380 (1965); (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[2] Representative polydentate ligands are illustrated in the recent papers: (a) G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967); (b) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967); (c) Z. Dori and H. B. Gray, *ibid.*, **88**, 1394 (1966); (d) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (e) L. Sacconi and I. Bertini, *J. Am. Chen. Soc.*, **88**, 5180 (1966).

[3] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

the structural data on $Co(PH(C_6H_5)_2)_3Br_2$,[4] $Ni(CN)_5{}^{3-}$,[5] and $Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$,[6] where the monodentate ligands exert no specific steric requirements. The last two and the $CuCl_5{}^{3-}$ ion are examples of a very limited number of five-coordinated complexes containing only one kind of unidentate ligand. These are of especial interest because of their simplicity.

On the basis of an earlier X-ray examination, which was based on visually estimated data and refined by trial and error,[7] the $CuCl_5{}^{3-}$ ion was assigned a trigonal-bipyramidal structure in which the axial Cu–Cl bond distance (2.32 Å) was "the same order of magnitude" as the equatorial Cu–Cl bond distance (2.35 Å). Mori and Fujiwara[8] then observed a symmetrical single-line electron paramagnetic resonance spectrum for $CuCl_5{}^{3-}$, and they interpreted the results in terms of five equal chlorine atoms. Subsequently, crystal field[9–11] and molecular orbital[12,13] calculations based on a trigonal-bipyramidal $CuCl_5{}^{3-}$ ion gave reasonable but not exceptionally good agreement with the observed electronic absorption spectrum of the $CuCl_5{}^{3-}$ ion. Recently, however, Adams and Lock[14] questioned the existence of the pentachlorocuprate(II) anion.

Since a symmetric five-coordinate $CuCl_5{}^{3-}$ ion would provide an ideal case for additional theoretical calculations[15] and because of the possibility of unequal axial and equatorial bond lengths in a trigonal-bipyramidal transition metal complex, an accurate determination of the crystal structure of $[Cr(NH_3)_6][CuCl_5]$ was undertaken. This study confirms that the $CuCl_5{}^{3-}$ ion is trigonal bipyramidal and that the equatorial Cu–Cl bonds are significantly longer than the axial Cu–Cl bonds, in contrast to what is expected on the basis of electrostatic or ligand–ligand repulsion arguments.[1b]

Determination of the Unit Cell and Collection of Intensity Data

Large yellow crystals of $[Cr(NH_3)_6][CuCl_5]$ were prepared as described previously.[7] The crystals were all octahedra or octahedral fragments. A series of precession photographs was taken with Cu Kα radiation, using a crystal approximately 0.8 mm in diameter. These photographs exhibited Laue symmetry m3m. The only systematic extinctions observed on overexposed photographs from this large crystal were: $hkl, h + k \neq 2n, k + l \neq 2n$; $hkl, l \neq 2n$; $0kl, k + l \neq 4n$. These extinctions are consistent only with space group $O_h{}^8$-Fd3c. Photographs were also taken along diagonals and at half-integer reciprocal lattice interplanar distances in an attempt to find additional zones. None was observed.

The single lattice constant was determined by least-squares refinement of the setting angles of 19 reflections that had been carefully centered on a Picker automatic X-ray diffractometer, using procedures previously described.[16,17] With the use of Mo Kα_1 radiation (λ 0.70930 Å) the lattice constant was found to be 22.240 (7) Å at 22°. This value is in good agreement with that of 22.265 (10) Å reported earlier.[7] For 32 formula units in the cell, the calculated density is 1.908 g/cm^3. This agrees very well with the observed density of 1.892 g/cm^3.[7]

Intensity data were collected in the manner previously described.[16,17] The crystal chosen for data collection was an octahedron, with an average trigonal face to trigonal face distance of 0.26 mm. The crystal was mounted so that the $1\bar{2}1$ axis was approximately along the spindle direction. In this way the effects of multiple reflections should be minimized.[18] The pulse height analyzer was set to admit about 90% of the Mo Kα window. The diffracted beams were filtered through 3.0 mils of Zr foil. The receiving aperture was 6 mm wide by 5 mm high and was positioned 30 cm from the crystal. A take-off angle of 1.5° was used; at this angle the heights of selected peaks were about 70% of their maximum values as a function of the take-off angle.

Data were collected by the θ–2θ technique at a scan rate of 1.0°/min. The scan was asymmetric to allow for the tails of the peaks on the high-angle side. The scan width was increased with scattering angle to account for the separation of the Kα_1 and Kα_2 peaks. The scan was taken from −0.60° from the 2θ value calculated for Kα_1 to +0.80° from the 2θ value calculated for Kα_2. Possible overlapping reflections were looked for, using procedures previously described.[19] The parameters employed were $\Delta_{\theta q} = 1.2$–$1.6°$, $\delta_v = 1.15°$.

For m3m symmetry independent reflections may be taken as $0 \leqslant h \leqslant k \leqslant l$. As a general check on crystal and electronic stability and in order to obtain more reliable results, dependent reflections were also observed.[20] The reflections $\bar{h}\bar{k}l$ and $h\bar{k}\bar{l}$ were collected out to $2\theta \leqslant 60°$. Additional reflections $l\bar{k}\bar{h}$ and $\bar{l}k\bar{h}$ were collected only for those reflections that had $I > 2\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation of the intensity I. A value of $p = 0.03$ was used in the calculation of these standard deviations.[16] Between 60 and 75° in 2θ the $\bar{h}\bar{k}l$ reflections were collected, and the additional three dependent reflections indicated above were collected if $I > 2\sigma(I)$. At higher angles there were very few peaks above background and these all had $h, k, l = 4n$. All four reflections described above were collected for such reflections be-

---

(4) J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966).

(5) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968).

(6) E. F. Riedel, J. G. Verkade, and R. A. Jacobson, to be submitted for publication. See Abstract P-10, American Crystallographic Association Meeting, Minneapolis, Minn., 1967.

(7) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

(8) M. Mori and S. Fujiwara, *ibid.*, **36**, 1636 (1963).

(9) P. Day, *Proc. Chem. Soc.*, 18 (1964).

(10) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

(11) G. C. Allen and N. S. Hush, *ibid.*, **6**, 4 (1967).

(12) W. E. Hatfield, H. D. Beldon, and S. M. Horner, *ibid.*, **4**, 1181 (1965).

(13) P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

(14) D. M. Adams and P. J. Lock, *ibid.*, *A*, 620 (1967).

(15) C. A. L. Becker, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1967.

(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(17) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(18) W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

(19) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).

(20) J. A. Ibers, *Acta Cryst.*, **22**, 604 (1967).

tween 75 and 90°. A total of 3347 reflections were observed; of these 759 were in the range $0 \leqslant I \leqslant \sigma(I)$ and 329 were in the range $\sigma(I) \leqslant I \leqslant 2\sigma(I)$. Standard reflections were measured periodically to test crystal stability. A very small uniform drop of 1.9% between the first standards and the last standards was found, and account was taken of this drop in bringing all reflections to a common scale.

The dimensions of the crystal were determined with the use of a micrometer eyepiece attached to a polarizing microscope. An absorption correction was then applied.[21] For a linear absorption coefficient of 33.6 cm^{-1} the transmission factors ranged from 0.45 to 0.53. The data were then averaged. The predicted weighted R factor on F^2 is 6.1%. Before absorption correction the value was 6.9%. The improvement is significant. A total of 1065 independent reflections were processed, of which 633 were greater than their standard deviations. These latter reflections we describe as being above background, and these reflections were used in the refinement of the structure.

Refinement of the Structure

Refinement of the structure was carried out by least-squares techniques. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The weights were taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors used were those tabulated by Ibers[22] for Cl and N, those of Cromer and Waber[23] for Cu and Cr, and those of Stewart, *et al.*,[24] for H. The effects of anomalous dispersion were included in the calculated structure factors.[25] The values of $\Delta f'$ and $\Delta f''$ for Cu, Cr, and Cl were those given by Cromer.[26]

The initial parameters were those reported earlier.[7] Refinement of the atomic positions and isotropic thermal parameters gave values of R_1 and R_2 (or weighted R factor) of 12.1 and 14.2%, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The poor agreement of this model is due primarily to the large anisotropy in the thermal vibrations of the equatorial Cl atom. Anisotropic refinement brought R_1 and R_2 down to 4.5 and 6.0%.

A difference Fourier map was computed after this refinement. The maximum electron density was 0.8 $e^-/\text{Å}^3$. The position of one hydrogen atom was clearly visible on it. The positions of the other two hydrogen atoms were deduced from geometrical considerations. A least-squares refinement with the hydrogens fixed at these positions gave values of R_1 and R_2 of 4.4 and 4.8%. This indicates a significant improvement in the model. The atomic scattering factors for the neutral and ionized species do not differ much, except below $\lambda^{-1} \sin \theta$ of 0.3 Å^{-1}. Owing to the large cell of the present compound, about 10% of the reflections are in this range. Accordingly, the calculation was repeated, but with atomic scattering factors for Cu^{2+}, Cr^{3+}, and Cl^- from the same tabulations. The values of R_1 and R_2 decreased to 4.3 and 4.4%. This is a significant improvement, as expected.

The hydrogen positions and their isotropic thermal parameters were then refined. The refinements converged normally, although the hydrogen atom thermal parameters were large (5–8 Å^2). With the use of neutral scattering factors the values of R_1 and R_2 were 3.7 and 3.4%. With the use of ionic scattering factors the corresponding values were 3.7 and 3.1%. Thus significant improvement is obtained on refinement of the hydrogen atom parameters.

An examination of the individual atomic contributions to the structure factors for the low-order reflections suggested that neither the neutral nor the ionic structure factors give optimum agreement. This is also chemically reasonable, since intuitively one does not expect the Cr atom to be fully +3 charged nor to be neutral. If f_n is the scattering factor for a neutral atom at a given value of $\lambda^{-1} \sin \theta$ and f_i is the corresponding ionic scattering factor, an interpolated intermediate scattering factor is given by $f = (1 - \alpha)f_n + \alpha f_i$. Here α is a measure of the charge on the atom in question. That is, if f_i is for the atom with a charge of q, f corresponds to an atom with charge $q\alpha$. Our least-squares program was modified to permit the refinement of values of α. In making these modifications account was taken of the relations among certain sets of derivatives.[27] If one assumes that the net charge of the complex is zero, that the axial and equatorial chlorine atoms have the same charge, and that the charge on the ions is ±3, then there are only two independent values of α to be determined. The refinement was effected by interpolation between Cr^0 and Cr^{3+}, Cu^0 and Cu^{2+}, Cl^0 and Cl^-, and N^0 and N^{3+}. The resultant charges were +1.00 (25) for Cr and +0.15 (20) for Cu. These lead to charges of +0.33 for N and −0.57 for Cl. Refinement of the charge parameters without the assumption that the ionic charges were ±3 always gave somewhat smaller ionic charges, but no significant changes in these parameters. For the final least-squares refinements, the ionic charge was taken as ±2.80, with charges of +1.00, +0.20, +0.30, and −0.60 on the Cr, Cu, N, and Cl atoms.[28] Such refinements converged to final values of R_1 and R_2

---

[21] In addition to various local programs for the CDC 3400 computer, local modifications of the following programs were employed: Hamilton's GONO9 absorption program; Zalkin's FORDAP Fourier program; the Busing–Levy ORFLS least-squares and ORFFE error function programs; and Johnson's ORTEP thermal ellipsoid plotting program.

[22] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[23] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[24] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[25] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

[26] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[27] For example, if $D_i = \partial F/\partial\alpha$ computed for $f = f_i$ and D_n is the analogous quantity for $f = f_n$, then $\partial F/\partial\alpha = D_i - D_n$ for the interpolated scattering factor. Additional constraints are imposed if the total charge is held constant. Further details on the program modifications, which are somewhat specific to our version of ORFLS, may be obtained from J. A. I.

[28] The interpretation of the chemical significance of the charges obtained by least-squares refinement should be made with recognition of the large standard deviations involved and the relatively few reflections which strongly affect these parameters. However, virtually all theoretical calculations of the charge density on metals in complexes show much smaller formal charges than given by their valence. This charge is expected to be diminished further if the complex has a net negative charge, if the metal is not very electropositive, and if the ligands are not very electronegative. Since Cr is very electropositive and Cu less so, the charges obtained are reasonable from a chemical point of view.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 2.5) FOR $[Cr(NH_3)_6][CuCl_5]$

K	L	FO	FC
***** H = 0 *****			
0	0	0	15958
0	4	5226	5296
0	8	863	820
0	12	3640	3626
0	16	3407	3442
0	20	877	925
0	24	826	852
0	28	959	986
0	32	471	489
0	36	454	457
0	40	357	369
0	44	111	115
2	2	289	253
2	6	500	491
2	10	450	451
2	14	1108	1094
2	22	746	754
2	30	321	327
2	38	108	97
4	4	3048	2926
4	8	1900	1908
4	12	2806	2849
4	16	2044	2112
4	20	1089	1128
4	24	1044	1072
4	28	843	870
4	32	454	450
4	36	365	357
4	40	325	310
4	44	192	172
6	6	362	387
6	10	757	739
6	14	810	808
6	18	309	323
6	22	579	590
6	26	147	131
6	30	241	245
6	34	113	73
8	8	4218	4104
8	12	2427	2452
8	16	855	699
8	20	1087	1102
8	24	1395	1397
8	28	808	824
8	32	290	280
8	36	281	250
8	40	300	299
10	10	183	150
10	14	891	897
10	22	665	683
10	26	126	127
10	30	247	262
12	12	2613	2600
12	16	1521	1528
12	20	627	941
12	24	1126	1147
12	28	764	765
12	32	254	247
12	36	335	333
12	40	328	313
14	14	467	474
14	18	514	525
14	22	333	344
16	16	1663	1691
16	20	901	927
16	24	493	496
16	28	480	468
16	32	495	480
16	36	393	379
16	40	174	180
18	22	393	390
18	30	183	187
20	20	779	775
20	24	412	389
20	28	436	411
20	32	463	445
20	36	222	233
22	22	133	101
22	26	192	173
24	24	695	665
24	28	508	498
24	32	142	160
24	36	115	139
28	28	314	295
28	32	155	131
***** H = 1 *****			
3	5	1159	1124
3	7	1668	1616
3	11	476	464
3	13	204	194
3	15	491	498
3	17	492	505
3	19	104	120
3	21	91	120
3	23	231	243
3	25	304	305
3	33	153	153
5	7	453	438
5	9	631	634
5	11	260	256
5	13	126	126
5	15	207	202
5	19	195	212
5	21	290	296
5	29	173	189
5	35	99	67
5	37	100	64
7	9	755	715
7	11	589	589
7	15	510	517
7	17	385	402
7	19	307	304
7	21	304	291
7	23	288	301
7	25	227	243
7	29	211	205
7	31	129	121
9	11	82	70
9	13	204	202
9	15	258	254
9	17	282	279
9	19	234	237
9	23	111	67
9	25	97	109
9	27	168	195
9	35	133	75
11	13	190	191
11	19	114	112
11	23	112	50
11	29	111	11
13	15	147	151
13	19	294	276
13	21	150	158
13	29	126	79
15	19	256	255
15	21	248	264
15	27	115	118
17	21	104	101
***** H = 2 *****			
2	2	1008	1008
2	4	303	303
2	6	425	411
2	8	927	926
2	10	387	399
2	12	504	507
2	14	1190	1163
2	18	256	274
2	22	128	127
2	24	224	235
2	30	98	70
2	32	143	123
4	4	755	744
4	6	154	159
4	8	1209	1169
4	10	401	399
4	12	271	278
4	14	359	357
4	16	610	622
4	18	249	244
4	20	442	460
4	22	277	277
4	24	265	302
4	28	445	452
4	30	145	150
4	32	146	153
4	36	225	206
6	6	847	845
6	8	474	459
6	10	267	255
6	12	314	324
6	14	545	560
6	16	138	128
6	18	201	205
6	22	196	184
6	24	215	219
6	28	102	115
6	32	128	140
6	36	129	98
8	8	115	107
8	10	1114	1079
8	12	518	519
8	14	493	496
8	16	154	159
8	18	421	425
8	22	225	236
8	30	135	58
10	10	681	653
10	12	433	418
10	14	166	173
10	16	157	169
10	18	449	455
10	24	203	223
10	26	349	350
10	34	201	226
12	12	127	125
12	14	120	111
12	16	291	300
12	18	154	165
12	20	299	300
12	24	223	218
12	28	283	272
12	32	114	129
14	14	953	960
14	16	433	434
14	20	139	104
14	22	194	194
14	24	222	238
14	26	138	130
16	16	225	224
16	22	323	325
16	28	120	86
16	30	176	189
18	18	386	380
18	26	277	290
20	20	226	238
20	22	124	113
26	26	151	148
***** H = 3 *****			
5	7	612	590
5	11	635	610
5	13	612	606
5	15	336	336
5	19	277	300
5	21	333	332
5	25	164	185
5	27	159	156
5	29	105	115
7	9	386	383
7	11	698	675
7	13	411	414
7	15	106	97
7	17	262	274
7	19	298	291
7	21	293	290
7	23	215	232
7	29	157	158
7	31	131	119
9	11	493	483
9	13	206	206
9	17	173	171
9	19	115	125
9	27	102	58
9	29	108	93
11	13	145	166
11	15	159	160
11	17	165	146
11	19	176	179
11	21	154	144
11	25	188	187
13	15	149	135
13	17	107	101
13	19	177	183
13	23	161	173
13	27	117	108
15	19	132	142
15	21	156	159
17	19	183	198
17	23	124	99
19	23	140	132
21	23	188	180
***** H = 4 *****			
4	4	3700	3623
4	6	3089	2986
4	8	3592	3534
4	10	1882	1804
4	12	2254	2304
4	14	719	717
4	16	1781	1837
4	18	811	822
4	20	1539	1566
4	22	189	192
4	24	921	951
4	26	395	427
4	28	667	668
4	32	600	602
4	36	382	368
4	40	243	221
6	6	246	241
6	8	238	234
6	12	1039	1027
6	14	195	195
6	16	179	180
6	18	94	64
6	20	370	384
6	22	103	92
6	24	130	121
6	34	139	9
8	8	3813	3732
8	12	1753	1799
8	14	456	454
8	16	1477	1516
8	18	159	156
8	20	1616	1644
8	24	843	869
8	28	548	547
8	32	611	613
8	36	349	360
8	40	189	183
10	10	392	388
10	12	907	901
10	14	275	286
10	16	131	129
10	18	174	182
10	20	372	389
10	22	316	321
10	28	178	183
12	12	1787	1806
12	14	440	431
12	16	1390	1407
12	18	636	636
12	20	970	982
12	22	165	183
12	24	869	887
12	26	350	357
12	28	632	634
12	30	127	44
12	32	388	381
12	36	343	333
12	40	251	251
14	16	396	400
14	18	234	246
14	20	283	280
14	24	192	195
14	28	199	198
16	16	1215	1211
16	18	209	220
16	20	941	939
16	22	163	137
16	24	698	695
16	28	502	495
16	32	395	385
16	36	297	296
16	40	217	194
18	18	191	195
18	20	369	365
18	22	139	163
18	28	242	230
18	30	138	123
20	20	942	938
20	24	493	489
20	26	209	210
20	28	390	377
20	32	414	405
20	36	235	223
24	24	478	471
24	28	401	390
24	32	271	235
24	36	157	179
28	28	254	275
28	32	187	176
***** H = 5 *****			
7	9	214	220
7	11	143	144
7	13	242	236
7	29	131	97
9	11	589	688
9	13	488	495
9	15	406	404
9	17	131	139
9	19	268	277
9	21	118	135
9	27	152	191
11	13	353	356
11	15	518	508
11	17	267	261
11	23	244	224
11	25	150	150
11	27	118	133
13	15	90	91
13	17	170	182
13	19	272	272
13	21	185	197
15	17	199	185
15	19	133	147
15	23	156	151
15	33	118	47
17	19	95	55
***** H = 6 *****			
6	6	1660	1615
6	8	381	353
6	10	103	87
6	12	321	342
6	14	111	91
6	16	195	187
6	18	1079	1095
6	22	320	324
6	24	220	226
6	26	530	554
6	28	131	141
6	34	182	169
8	8	395	387
8	10	634	628
8	14	515	518
8	16	240	243
8	18	344	342
8	20	170	167
8	22	411	415
8	24	111	117
8	28	136	126
8	30	178	151
10	10	205	204
10	12	147	129
10	14	218	243
10	16	204	196
10	18	612	612
10	24	175	184
10	26	327	341
12	12	404	408
12	14	148	136
12	16	78	107
12	20	181	187
14	14	87	96
14	16	407	406
14	18	362	383
14	20	148	121
14	22	103	80
14	24	231	231
14	26	148	119
16	16	229	241
16	22	311	320
16	24	126	126
16	28	140	134
16	30	150	164
18	22	180	187
18	26	148	38
20	20	217	223
20	22	104	73
22	24	144	151
24	28	145	117
***** H = 7 *****			
9	11	243	236
9	13	185	180
9	15	251	263
9	25	167	168
11	13	86	84
11	15	297	299
11	17	182	185
11	23	146	161
11	25	150	148
13	15	268	261
13	17	220	214
13	23	202	223
13	27	75	76
15	17	150	141
15	21	115	135
15	23	141	155
15	25	99	49
17	25	116	133
19	25	115	96
***** H = 8 *****			
8	8	2051	2098
8	10	115	102
8	12	1153	1214
8	16	2056	2103
8	18	153	159
8	20	1711	1760
8	22	213	227
8	24	331	341
8	28	350	368
8	32	833	820
8	36	431	431
8	40	138	109
10	10	1040	1025
10	14	355	405
10	16	155	147
10	18	332	339
10	20	162	137
10	24	125	113
12	12	1485	1501
12	14	169	168
12	16	1418	1435
12	18	125	159
12	20	913	926
12	24	670	669
12	28	590	589
12	32	454	434
12	36	304	292
12	40	205	212
14	14	538	548
14	18	170	154
14	20	100	82
14	22	393	395
14	30	204	215
16	16	691	679
16	18	151	138
16	20	769	765
16	22	150	126
16	24	924	911
16	28	572	558
16	32	225	233
16	36	229	194
16	40	252	225
18	18	195	217
18	22	120	107
20	20	914	914
20	24	573	568
20	28	357	350
20	32	316	332
20	36	218	217
22	22	376	378
22	30	162	142
24	24	281	271
24	26	119	2
24	28	304	283
24	32	315	303
24	36	221	216
28	28	265	257
28	32	235	208
***** H = 9 *****			
11	13	246	261
11	15	310	334
11	17	305	287
11	19	156	135
11	21	133	112
11	23	199	181
11	25	198	219
11	27	141	116
11	33	109	91
13	17	279	279
13	19	184	178
15	17	154	152
15	19	109	18
17	19	233	235
17	27	159	148
***** H = 10 *****			
10	10	276	263
10	12	578	577
10	14	394	399
10	16	149	192
10	18	427	426
10	22	138	114
10	24	221	234
10	26	229	234
12	12	559	552
12	18	252	259
12	20	252	255
12	24	90	41
12	26	110	102
12	28	166	161
14	16	338	333
14	18	338	360
14	24	217	209
14	26	189	188
16	16	235	218
16	20	113	117
16	22	226	244
16	24	132	151
18	18	211	206
18	20	158	125
18	22	135	143
18	32	110	11
20	20	178	198
20	28	142	120
22	26	134	157
24	24	125	135
***** H = 11 *****			
13	15	217	210
13	17	93	22
13	19	161	149
15	21	125	125
17	21	110	95
***** H = 12 *****			
12	12	2125	2103
12	14	219	204
12	16	1418	1425
12	18	506	490
12	20	590	596
12	22	107	126
12	24	795	780
12	26	302	308
12	28	682	685
12	32	276	269
12	36	233	229
12	40	273	245
14	14	129	132
14	20	179	171
14	26	140	137
16	16	855	860
16	18	189	184
16	20	559	576
16	24	698	698
16	28	530	526
16	32	259	254
16	36	259	223
18	20	257	282
18	24	123	96
18	28	163	154
20	20	618	617
20	24	452	448
20	26	130	164
20	28	358	338
20	32	316	308
20	36	219	221
24	24	388	372
24	28	339	326
24	32	247	230
28	28	274	264
28	32	158	158
***** H = 13 *****			
15	17	105	94
17	19	176	191
17	21	131	147
19	23	107	108
***** H = 14 *****			
14	14	382	398
14	16	291	294
14	18	99	81
14	24	223	216
16	16	227	229
16	18	211	204
16	22	259	250
18	18	173	165
20	20	137	152
22	24	136	124
***** H = 15 *****			
17	21	134	117
***** H = 16 *****			
16	16	1032	1049
16	18	172	162
16	20	698	679
16	24	353	343
16	28	337	330
16	32	382	369
16	36	395	265
18	22	136	108
20	20	668	634
20	24	338	339
20	26	123	68
20	28	275	261
20	32	327	302
20	36	229	203
22	22	139	136
22	24	121	17
24	24	461	444
24	28	335	317
24	32	155	149
28	28	263	249
***** H = 18 *****			
18	18	244	216
18	22	153	152
18	26	225	195
20	22	165	136
***** H = 20 *****			
20	20	671	638
20	24	350	346
20	28	210	201
20	32	246	223
24	24	327	311
24	28	260	215
***** H = 24 *****			
24	24	224	186
24	28	342	364

TABLE II

ATOMIC PARAMETERS FOR $[Cr(NH_3)_6][CuCl_5]$

Atom	Position	Site symmetry	x	y	z	β_{11}[a] or B[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	32c	S_6-$\bar{3}$	0	0	0	777 (5)	β_{11}	β_{11}	−35 (7)	β_{12}	β_{12}
Cu	32b	D_3-32	$^1/_4$	$^1/_4$	$^1/_4$	1159 (6)	β_{11}	β_{11}	−77 (7)	β_{12}	β_{12}
Cl_{ax}	64e	C_3-3	0.190387 (26)	x	x	1286 (8)	β_{11}	β_{11}	−127 (9)	β_{12}	β_{12}
Cl_{eq}	96g	C_2-2	$^1/_4$	0.076026 (32)	$-y$	4570 (44)	1120 (11)	β_{22}	640 (17)	β_{12}	184 (15)
N	192h	C_1-1	0.07113 (11)	0.05139 (13)	−0.03026 (13)	978 (44)	1406 (56)	1473 (53)	−171 (39)	59 (38)	116 (41)
H_1			0.062 (2)	0.085 (2)	−0.038 (2)	8.3 (14)					
H_2			0.082 (1)	0.041 (2)	−0.059 (1)	4.4 (10)					
H_3			0.095 (2)	0.050 (2)	−0.012 (1)	4.5 (10)					

[a] Multiplied by 10^6. The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic temperature factor in Å^2.

of 3.7 and 3.1%. The ratio of the value of R_2 in this model to that for the fully ionic model is 0.99. In effect only two additional parameters are involved and so the improvement is probably significant. There was marked improvement in some of the low-angle reflections, but, of course, no change in most of the reflections.

Attempts to refine the hydrogen atoms with anisotropic thermal parameters reduced R_1 and R_2 to 3.5 and 2.9%, but generally one or more of the hydrogen ellipsoids was nonpositive definite. Examination of the ellipsoid orientations showed that they were longer in the direction expected for NH_3 rotation. That is, this may be a case of a severely hindered rotor. The motion of the hydrogen atoms gives an electron density cloud (or probability envelope) that is shaped like a banana, with the Cr–N bond the oscillation axis. An ellipsoidal shape is not, apparently, an adequate approximation.

The final error in an observation of unit weight is 0.94, which indicates that the value of p of 0.03[16] chosen for the determination of individual standard deviations of the intensities is a reasonable one. An error analysis as a function of scattering angle, F_o, and indices shows no unusual trends. The final calculated value of R_2 on F^2 is 6.2%, in excellent agreement with that predicted from the averaging of the observations. There is no evidence for extinction effects in the data.

Final values of the observed and calculated structure amplitudes are given in Table I. These may be brought to an absolute scale in electrons by dividing by 2.5. None of those reflections for which $I < \sigma(I)$ had $|F_c|$ greater than $1.5|F_o|$. The final values of the atomic parameters along with their standard deviations estimated from the inverse matrix are given in Table II. Table III lists the important bond distances and angles that may be derived from these parameters.

Description of Structure

The salt consists of discrete $Cr(NH_3)_6{}^{3+}$ and $CuCl_5{}^{3-}$ ions. The $CuCl_5{}^{3-}$ ion is a regular trigonal-bipyramidal five-coordinated complex (Figure 1). The axial bond length of 2.2964 (12) Å is significantly shorter than the equatorial bond length of 2.3912 (13) Å. The difference is 0.0948 (14) Å.

The crystallographic site symmetry is 32, but the symmetry of the $CuCl_5{}^{3-}$ ion as given by the atom positions is rigorously $\bar{6}m$. The lower symmetry of

TABLE III

BOND LENGTHS AND ANGLES IN $[Cr(NH_3)_6][CuCl_5]$

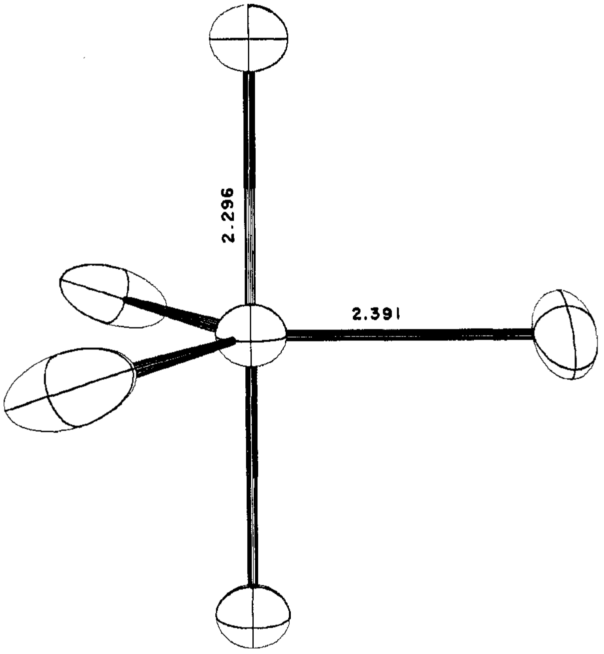
Bond	Distance, Å	Atoms	Angle, deg
$Cu-Cl_{ax}$	2.2964 (12)	N-Cr-N	89.65 (12)
$Cu-Cl_{eq}$	2.3912 (13)		
Difference	0.0948 (14)	$Cr-N-H_1$	113[a]
		$Cr-N-H_2$	111
Cr-N	2.0644 (25)	$Cr-N-H_3$	113
$N-H_1$	0.80 (5)	$Cr-N\cdots Cl_{ax}$	116.46 (8)
	0.72 (3)	$Cr-N\cdots Cl_{eq}$	98.34 (8)
	0.67 (3)	$Cr-N\cdots Cl_{eq}$	100.95 (8)
$N\cdots Cl_{ax}$	3.3262 (30)	$Cu-Cl_{ax}\cdots H$	94
$N\cdots Cl_{eq}$	3.3962 (33)	$Cu-Cl_{eq}\cdots H$	134
$N\cdots Cl_{eq}$	3.3122 (32)	$Cu-Cl_{eq}\cdots H$	108
		$N-H_3\cdots Cl_{ax}$	172
		$N-H_2\cdots Cl_{eq}$	157
		$N-H_1\cdots Cl_{eq}$	160

[a] No error estimate is assigned to bond angles involving the H atoms because the positions of the H atoms are systematically in error, as discussed in the text.

the ion in the lattice, as shown in Figure 1, is due entirely to the asymmetric nature of the vibrational and librational modes of the complex ion which, in turn, are caused by asymmetric perturbations of the environment. That is, the environment of the complex does not have $\bar{6}$m symmetry; hence the vibrational modes of the complex cannot have symmetry this high.

The orientation of the thermal ellipsoids for the chlorine atoms can be seen in Figure 1, and the root-mean-square amplitudes of vibration along the principal axes are given in Table IV. The axial chlorine atom is only slightly anisotropic with a root-mean-square amplitude of vibration of 0.1609 (15) Å along the $Cu-Cl_{ax}$ bond and an amplitude of 0.1881 (9) Å normal to this bond. The copper atom is also only slightly anisotropic with an amplitude of vibration of 0.1587 (11) Å along the threefold axis and an amplitude of 0.1760 (8) Å normal to this.

The equatorial chlorine atom, as mentioned earlier, is very anisotropic. The amplitude of vibration along the $Cu-Cl_{eq}$ bond is 0.1532 (14) Å, and the amplitude normal to this bond and in the $Cu-Cl_{ax}$ direction is 0.1637 (14) Å. However, the amplitude of vibration that is nearly in the equatorial plane and is normal to the $Cu-Cl_{eq}$ bond is much larger, 0.3469 (17) Å. The angle between this ellipsoid axis and the equatorial plane is 20.76 (34)°. It is impossible to say whether this motion is due to a libration around the threefold axis (*i.e.*, the equatorial chlorine atoms move in a more or less concerted fashion in this direction) or to an independent, very anisotropic vibration. An anisotropic vibration of the equatorial chlorine atom is consistent with the electronic spectral results of Allen and Hush.[11] On the basis of the temperature dependence of the ligand field transition maxima, they predicted that the equatorial bond is more affected by a decrease in temperature than the axial bond. However, their argument that the lattice contraction *per se* shortens the equatorial Cu-Cl bond length more than the axial Cu-Cl bond length is incorrect. A cubic lattice is, by definition, isometric, and, assuming that fractional coordinates remain constant, a lattice contraction causes a uniform shift in all bonds whatever their orientation. The only way to test the hypothesis that the equatorial Cu-Cl bond contracts more than the axial bond on cooling is to determine the changes in fractional coordinates.



$CuCl_5^{3-}$

Figure 1.—A perspective drawing of the $CuCl_5^{3-}$ ion in $[Cr(NH_3)_6][CuCl_5]$. The shapes of the atoms in this and following drawings, unless noted otherwise, represent 50% probability contours of thermal motion.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL THERMAL ELLIPSOID AXES

Atom	Axis 1, Å	Axis 2, Å	Axis 3, Å
Cu	0.1587 (11)	0.1760 (8)	0.1760 (8)
Cr	0.1330 (14)	0.1426 (8)	0.1426 (8)
Cl_{ax}	0.1609 (15)	0.1881 (9)	0.1881 (9)
Cl_{eq}	0.1532 (14)	0.1637 (14)	0.3469 (17)
N	0.1503 (35)	0.1865 (36)	0.1981 (34)

The axial and equatorial Cu-Cl bond lengths corrected for the effects of thermal motion[29] are: riding model, 2.298, 2.410 Å; independent model, 2.325, 2.434 Å. Note that the difference in bond lengths is relatively independent of the thermal model chosen and remains highly significant.

The $\bar{3}$ site symmetry (Figure 2) of the $Cr(NH_3)_6^{3+}$ cation is the highest symmetry this complex can have without fixing the angular orientation of the NH_3 groups. (There is one orientation, when an N-H bond is coplanar with the $\bar{3}$ axis, where the symmetry can be $\bar{3}$m, which has $\bar{3}$ as a subgroup.) The coordination geometry is very nearly "octahedral" with an N-Cr-N angle of 89.65 (12)°. The Cr-N bond length is 2.0644 (25) Å.

The orientation of the hydrogen atoms minimizes the nonbonded H-H interactions (Figure 3). The

---

(29) W. R. Busing and H. A. Levy, *Acta Cryst.*, **17**, 142 (1964).

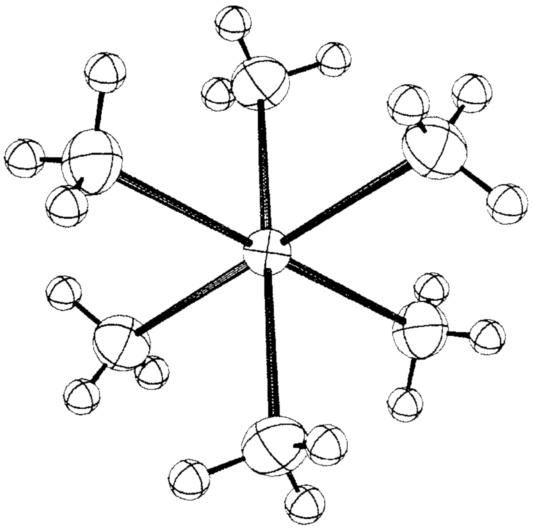


Figure 2.—A perspective drawing of the $Cr(NH_3)_6^{3+}$ ion in $[Cr(NH_3)_6][CuCl_5]$ as viewed down the crystallographic $\bar{3}$ (S_6) axis. The isotropic thermal factor used for the H atoms in this and the following diagram was chosen as 1.0 Å^2 for clarity.

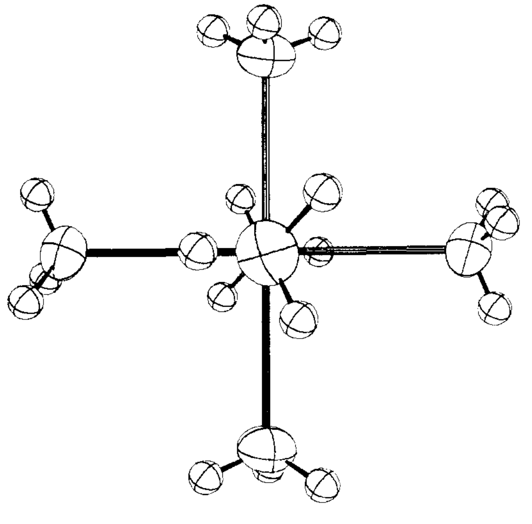


Figure 3.—A perspective drawing of the $Cr(NH_3)_6^{3+}$ ion as viewed down a Cr–N bond.

calculated N–H bond lengths are 0.802 (55), 0.717 (32), and 0.672 (33) Å. X-Ray results tend to give short N–H or C–H bond lengths.[30] However, in this structure the compression of the N–H bond lengths from the effect of oscillation (fitting a banana shape with a sphere) is probably more important. The Cr–N–H angles are 113 (3), 111 (3), and 113 (3)°. The contraction of the N–H bond length acts to make these angles systematically too large.

The closest N–H···Cl interactions are only slightly less than the sum of van der Waals radii, depending upon the value chosen for nitrogen. In any event, the N–H···Cl hydrogen bonds are weak.

Discussion

For a five-coordinate complex formed from equivalent unidentate ligands, ligand–ligand electron repulsion is minimized in a trigonal-bipyramidal geometry. In the absence of other stereochemical effects, therefore, one expects to find trigonal-bipyramidal rather than square-pyramidal geometry for ML_5 complexes. This is true, for example, for PF_5 and PCl_5 in the gaseous state. However, there is a relatively small distortion required to interconvert the two geometries and the energy difference between them is expected to be very small. This is supported by the rapid intramolecular ligand exchange of PF_5 and related compounds and by the recent isolation of both geometries for the $Ni(CN)_5^{3-}$ ion.[5,31] In addition, although the $CuCl_5^{3-}$ ion is trigonal bipyramidal, the $MnCl_5^{2-}$ ion is square pyramidal.[32]

The stereochemical activity of the metal 3d electrons acts to stabilize further the square-pyramidal form relative to the trigonal bipyramid. This stabilization is predicted by crystal field theory calculations.[33] These calculations are more or less equivalent to the explanation offered by Gillespie,[34] who considered the interactions of asymmetric metal d-electron clouds with ligand electron pairs. For most distributions of metal d electrons this interaction favors the square-pyramidal form. However, when there is appreciable electron delocalization in the metal–ligand bond (*i.e.*, appreciable covalent bonding) the trigonal-bipyramidal geometry is favored.

Because of the nonspherical character of the electron density in the d orbitals of transition metals, it is important to determine if a trigonal-bipyramidal ML_5 complex has different axial and equatorial bond lengths. The five trigonal-bipyramidal ML_5 complexes studied to date are listed in Table V. The early structural studies seem to indicate that the axial bond length is in fact shorter than the equatorial, but the differences in bond lengths, even for the recently reported $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$ cation, are never more than two or three standard deviations. The trigonal-bipyramidal $Ni(CN)_5^{3-}$ ion is the first case in which the axial bond is reliably shorter than the equatorial bond, but the distorted geometry of the anion leaves the situation still ambiguous. However, the bond lengths of the regular trigonal-bipyramidal $CuCl_5^{3-}$ complex unequivocally show that the axial bond lengths are shorter than equatorial ones.

The contraction of the axial bond length relative to the equatorial for a trigonal-bipyramidal low-spin d^8 or d^9 complex was predicted by Gillespie[34] on the basis of the electron-pair-repulsion model described earlier.

By dividing the electron repulsions of a transition

---

(30) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

(31) K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 949 (1966).

(32) I. Bernal, private communication.

(33) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967.

(34) R. J. Gillespie, *J. Chem. Soc.*, 4679 (1963).

TABLE V

AXIAL AND EQUATORIAL M–L BOND LENGTHS OF TRIGONAL-BIPYRAMIDAL COMPLEXES WITH FIVE IDENTICAL LIGANDS

Complex	d^x	Axial, Å	Equatorial, Å	Ref
$Fe(CO)_5$	d^8	1.81 (2)	1.79 (2)	*a, b, c, d*
$Co(CNCH_3)_5{}^+$	d^8	1.84 (2)	1.88 (2)	*e*
$Ni(CN)_5{}^{3-}$	d^8	1.838 (9)	1.94[f]	*g*
$Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$	d^8	2.14 (1)	2.19 (1)	*h*
$Pt(SnCl_3)_5{}^{3-}$	d^8	?	?	*i*
$CuCl_5{}^{3-}$	d^9	2.2964 (12)	2.3912 (13)	*j*

[a] A. W. Hanson, *Acta Cryst.*, **15,** 930 (1962). [b] J. Donohue and A. Caron, *ibid.*, **17,** 663 (1964). [c] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69,** 3405 (1965). [d] J. Donohue and A. Caron, *ibid.*, **70,** 603 (1966). [e] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4,** 318 (1965). [f] This is an average of chemically nonequivalent bonds. [g] Reference 5. [h] Reference 6. [i] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87,** 658 (1965). [j] This work.

metal complex into ligand–ligand repulsions and d-electron–ligand repulsions one can examine the effects of various d-electron distributions on the geometry of the complex. From the ligand–ligand repulsions one always predicts the axial bond to be longer than the equatorial. However, the d-electron–ligand repulsions can favor either axial contraction or elongation, depending upon the d-electron configuration. For a low-spin d^8 or d^9 complex the metal 3d-electron density distribution is an *oblate* spheroid, since the d_{z^2} orbital is either empty or only half-filled. The metal–ligand electron repulsion along the trigonal (z) axis is therefore weakened and equilibrium is achieved at a shorter axial bond length than if the d-electron shell had spherical symmetry. The difference between axial and equatorial bond lengths is expected to be most pronounced for relatively ionic complexes with small ligands. The more covalent the metal–ligand bond and the larger the ligands, the more important the ligand–ligand repulsions become, with a concomitant lengthening of the axial bond.

A similar result can be formulated by using a molecular orbital model with either σ orbitals or both σ and π atomic orbitals. However, the additional sophistication of this model is not, to date, justified by greater predictive powers.

Acknowledgment.—K. N. R. wishes to express his gratitude to the National Institutes of Health for a predoctoral fellowship. D. W. M. wishes to express his thanks to The Ohio State University for a research leave. We are grateful to the National Science Foundation for their support of this work.

CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

Base Adducts of Bis(2,4-pentanedionato)cobalt(II). The Crystal and Molecular Structure of *trans*-Bis(2,4-pentanedionato)dipyridinecobalt(II), $Co(AA)_2(py)_2$

BY R. C. ELDER

Received December 13, 1967

A series of pyridine and water adducts to bis(2,4-pentanedionato)cobalt(II), $Co(AA)_2$, where the common name of acetylacetone is abbreviated AA, is reported. From crystallographic evidence these are *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II), $Co(AA)_2(py)_2$ (orthorhombic, $a = 11.13$, $b = 16.18$, $c = 11.91$ Å, space group C_{mcm}, $z = 4$, measured density 1.28 g cm^{-3}, calculated density 1.29 g cm^{-3}), tetrakis(2,4-pentanedionato)pyridinedicobalt(II), $[Co(AA)_2py]_2$ (triclinic, $a = 9.70$, $b = 11.61$, $c = 15.03$ Å, $\alpha = 103° 35'$, $\beta = 103° 40'$, $\gamma = 92° 15'$, $z = 2$, measured density 1.40 g cm^{-3}, calculated density 1.40 g cm^{-3}), and tetrakis(2,4-pentanedionato)pyridineaquodicobalt(II), $[Co(AA)_2]_2pyH_2O$ (triclinic, $a = 8.84$, $b = 9.42$, $c = 17.37$ Å, $\alpha = 92° 30'$, $\beta = 96° 15'$, $\gamma = 95° 45'$, $z = 2$, measured density 1.38 g cm^{-3}, calculated density 1.41 g cm^{-3}). No crystals of the reported compound tetrakis(2,4-pentanedionato)pyridinedicobalt(II), $[Co(AA)_2]_2py$, were obtained. The structure of $Co(AA)_2(py)_2$ has been determined from three-dimensional, single-crystal X-ray data obtained on a Pailred diffractometer. The structure, refined by least-squares methods to a final conventional R factor for nonzero data of 0.047 and wR (all data) of 0.048, has molecular symmetry mm. All atoms including hydrogen were found and refined. The configuration of the molecule is that of the *trans*-dipyridine adduct with the planes of the two pyridine rings at 90° to each other. Both the molecular conformation and the cobalt–nitrogen atom bond lengths suggest the possibility of metal–nitrogen π bonding.

Introduction

Studies of the adducts of bis(2,4-pentanedionato)cobalt(II), $Co(AA)_2$, where the common name of the acetylacetonate ligand $C_5H_7O_2{}^-$ has been abbreviated AA, with donors[1–4] such as water, pyridine, and cyclohexylamine have shown these compounds to be derived from the structure of the anhydrous tetramer,[5] $[Co(AA)_2]_4$. The tetramer (see Figure 1) is formed of four cobalt–oxygen octahedra, where the central bridge

---

(1) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **5,** 423 (1966).

(2) F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **90,** 38 (1968).

(3) J. P. Fackler, Jr., *Inorg. Chem.*, **2,** 266 (1963).

(4) J. A. Bertrand, F. A. Cotton, and W. J. Hart, *ibid.*, **3,** 1007 (1964).

(5) F. A. Cotton and R. C. Elder, *ibid.*, **4,** 1145 (1965).