composed when ground with KBr powder, mineral oil, or Halocarbon oil in the drybox.) Oxidizing power was determined iodometrically. X-Ray powder patterns of the final product were obtained with a 114.59-mm diameter Philips camera and copper Kα radiation.

Results and Discussion

Figure 1A shows the infrared spectrum from 300 to 1200 cm^{-1} of the solid at the end of the first 3 hr of fluorination. The band at 673 cm^{-1} is ascribed to $Ni(ClF_2)_2$ and the band at 758 cm^{-1} to $Ni(ClF_4)_2$. The difluorochlorate anion, ClF_2^-, absorbs at 635, 636, and 661 cm^{-1} in the compounds $NOClF_2$, $CsClF_2$, and $RbClF_2$, respectively.[2] The tetrafluorochlorate anion, ClF_4^-, absorbs at 742 and 745 cm^{-1} in $CsClF_4$ and $RbClF_4$, respectively.[3] At this stage of fluorination, the solid had an oxidizing power of approximately 0.45 equiv of iodine/mol of nickel. The solid fumed on exposure to air, and the initial brown color faded quickly to pale yellow. Henkel and Klemm[4] obtained a similar product from the fluorination of nickel dichloride, which they considered to be a mixture of NiF_2 and NiF_3 or NiF_4. Although the brown color is indicative of at least a small percentage of nickel(III) in the product at this stage, the oxidizing power and the low nickel content[4] can be more readily ascribed to the presence of ClF_2^- and ClF_4^-.

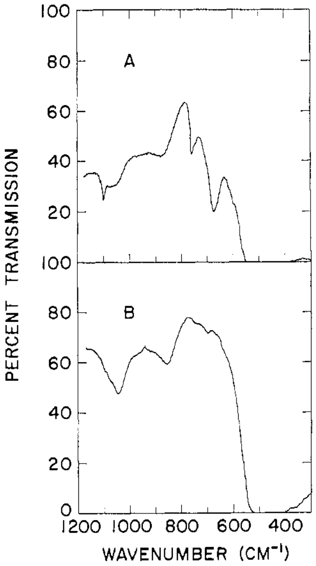


Figure 1.—Infrared spectra of solids obtained from the fluorination of nickel dichloride at 150–200°: (A) product after 3 hr of fluorination; (B) product after 9 hr of fluorination (dry powders).

After 6 hr more of fluorination, the oxidizing power dropped to approximately 0.07 equiv of iodine/mol of nickel, and the solid no longer fumed in air. Broad bands at 855 and 1045 cm^{-1} became more prominent in the infrared spectrum, as shown in Figure 1B, whereas the fluorochlorate bands disappeared. In both Figures 1A and 1B, the major product, nickel difluoride, produced the very strong band from 400 to 550 cm^{-1} (off scale in the figures). The following equations show the formation and decomposition of the transient nickel fluorochlorate compounds

$$NiCl_2 + 2F_2 \longrightarrow Ni(ClF_2)_2$$

$$Ni(ClF_2)_2 + 2F_2 \longrightarrow Ni(ClF_4)_2$$

$$Ni(ClF_2)_2 \longrightarrow NiF_2 + 2ClF$$

$$Ni(ClF_4)_2 \longrightarrow NiF_2 + 2ClF_3$$

The infrared bands at 855 and 1045 cm^{-1} disappeared when the solid was exposed to humid air for several minutes and reappeared when the solid was again fluorinated. X-Ray powder photographs of the solid showed only lines of the major phase, tetragonal nickel difluoride.[5] The compound producing the 855- and 1045-cm^{-1} bands has not been identified thus far. It appears unlikely that this compound is nickel trifluoride, since the frequencies of both bands are too high to be ascribed to nickel–fluorine stretching vibrations. In the complex salts K_3NiF_6 and K_2NiF_6 (which have anions of O_h symmetry), vibration ν_3 occurs at 580 and 663 cm^{-1}, respectively, and in cobalt trifluoride, ν_3 occurs at 565 cm^{-1}. Since stretching vibrations of doubly bound oxygen generally occur in the region 800–1100 cm^{-1} and since bending modes of hydrogen fluoride in acid salts also occur in this region, an unstable oxyfluoride or acid fluoride of nickel(III) is a much more probable source of the two bands.

Acknowledgment.—We are greatly indebted to B. Tani for X-ray powder photographs of the solids.

---

[2] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6**, 1159 (1967).

[3] K. O. Christe and J. P. Guertin, *ibid.*, **5**, 473 (1966).

[4] P. Henkel and W. Klemm, *Z. Anorg. Allgem. Chem.*, **222**, 73 (1935).

[5] J. W. Stout and S. A. Reed, *J. Am. Chem. Soc.*, **76**, 5279 (1954).

CONTRIBUTION FROM THE
TRANSURANIUM RESEARCH LABORATORY, CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE 37831

The Crystal Structure of Cesium Tetrakis(hexafluoroacetylacetonato)europate and -americate. Isomorphism with the Yttrate[1]

BY JOHN H. BURNS AND M. D. DANFORD

Received December 2, 1968

The publication of a preliminary report on the structure of $CsY(HFA)_4$ (where HFA = hexafluoroacetylacetone) by Lippard, Cotton, and Legzdins[2] led us to extend the study of this type of compound to some lanthanide and transuranic elements[3] and to a complete analysis of the crystal structures[4] of $CsEu(HFA)_4$ and

---

[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

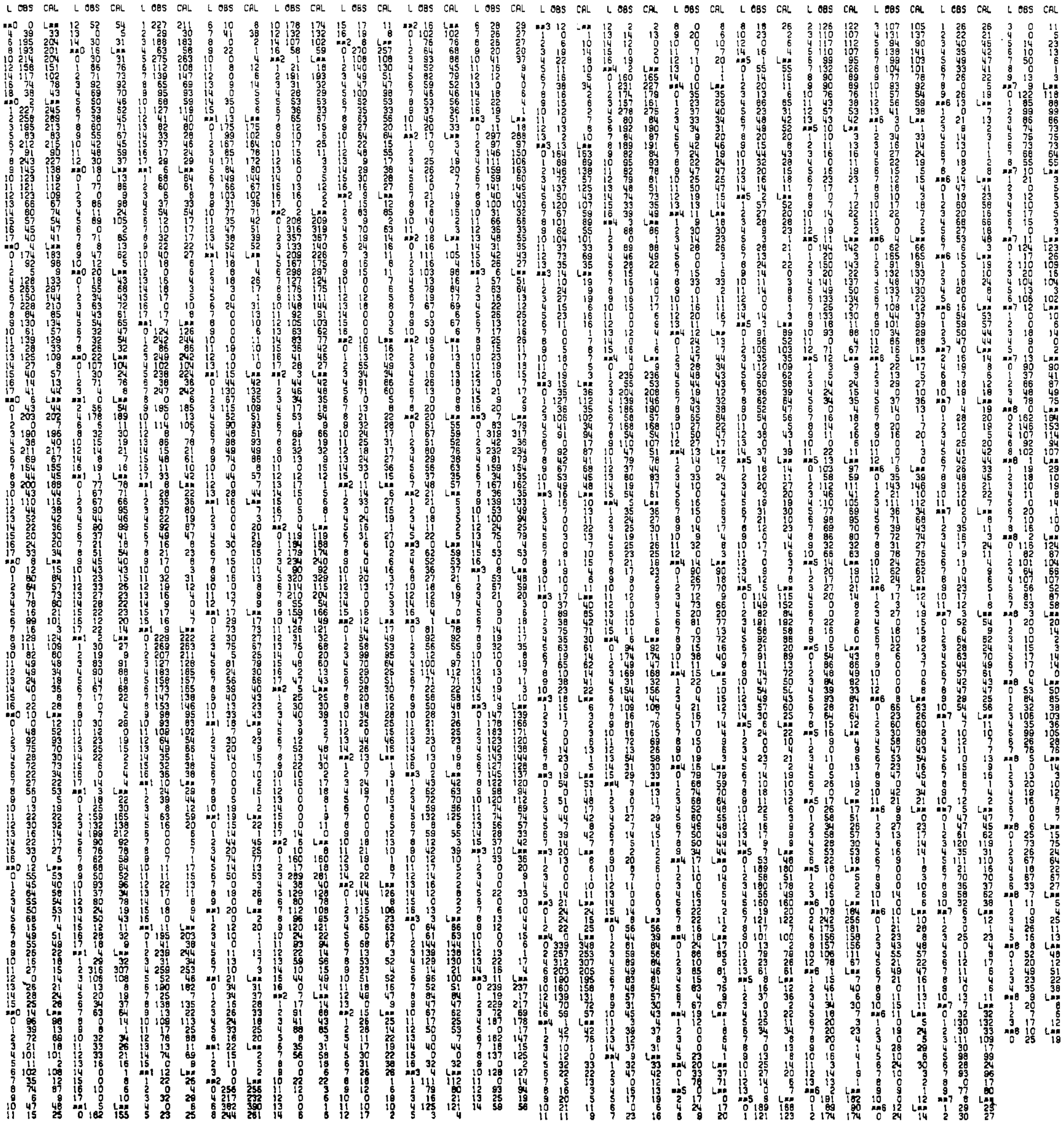
[2] S. J. Lippard, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **88**, 5930 (1966).

[3] M. D. Danford, J. H. Burns, O. L. Keller, J. R. Stokely, and W. H. Baldwin, to be submitted for publication.

[4] J. H. Burns and M. D. Danford, Abstracts, American Crystallographic Association Meeting, Buffalo, N. Y., Aug 11–16, 1968, Paper D10.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $CsEu(HFA)_4$ ON AN ABSOLUTE SCALE[a]



[a] Column headings: L, Miller index *l*; OBS, observed structure factor; CAL, calculated structure factor.

$CsAm(HFA)_4$. A subsequent paper by Bennett, Cotton, Lippard, and Legzdins[5] presented the details of a more precise determination of the crystal structure of $CsY(HFA)_4$ based on counter-measured X-ray data. Our independently determined structures are in close agreement with theirs, indicating that the compounds are isomorphous; hence we are presenting our results in abbreviated form in order that the three structures may be compared.

Experimental Section

Compound Preparation.—The compounds were prepared by reaction of $EuCl_3$ and $AmCl_3$, respectively, with Cs(HFA) in aqueous ethanol, as described previously.[6] The isotope ^{243}Am was used in the preparation of $CsAm(HFA)_4$ and glove boxes were required for all of its manipulations. The original precipitate from ethanol was monoclinic $CsAm(HFA)_4 \cdot H_2O$, which was shown[3] to have isomorphous analogs when the central ion is Pr, Nd, or Cm; but for Eu only the anhydrous, orthorhombic $CsEu(HFA)_4$ was obtained. Suitable crystals for X-ray study of the orthorhombic form of $CsEu(HFA)_4$ and $CsAm(HFA)_4$ were prepared by recrystallization from 1-butanol followed by washing with toluene; these crystals were in the form of thick plates and were pale yellow and pale rose, respectively. The α-active ^{243}Am was contained by sealing its compound in a thin-walled glass capillary tube.

Data Collection.—Precession photographs were used to obtain the pattern of systematic absences: $hk0$ for $h + k \neq 2n$, $0kl$ for $k \neq 2n$, and $h0l$ for $l \neq 2n$, which are characteristic of space group Pbcn and indicated isomorphism of the compounds with $CsY(HFA)_4$. Unit-cell and intensity data were collected by a computer-controlled Picker X-ray diffractometer using Mo Kα radiation and a scintillation-counter detector. Intensities were collected by θ–2θ scans and the backgrounds were measured at the two ends of the scans and averaged. A reference reflection was measured frequently to monitor the beam intensity and to follow the effect of self-radiolysis, which diminished the scattering power of the radioactive sample by about 25% during the

---

(5) M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, *Inorg. Chem.*, **7**, 1770 (1968).

(6) S. J. Lippard, *J. Am. Chem. Soc.*, **88**, 4300 (1966).

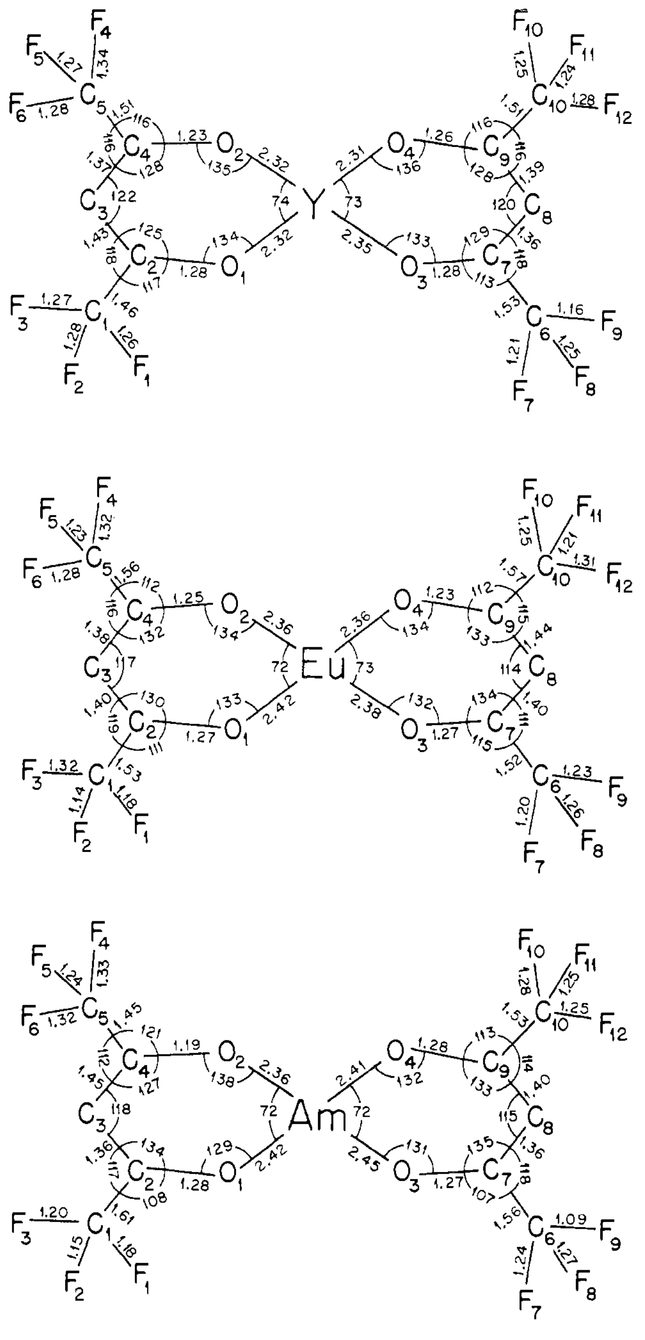


Figure 1.—Comparison of bond lengths and angles in CsY(HFA)$_4$, CsEu(HFA)$_4$, and CsAm(HFA)$_4$. Average standard errors of these quantities are given in the text.

several days of data collection. Some 1893 independent reflections were measured for CsEu(HFA)$_4$ and 1036 for CsAm(HFA)$_4$.

Calculations.—Absorption corrections were calculated with the ORABS program.[7] For this purpose the crystals were described as being bounded by planes. Seven planes were used to describe the platelike crystal of CsEu(HFA)$_4$ which had maximum and minimum dimensions of 0.26 and 0.11 mm, respectively. The CsAm(HFA)$_4$ sample, also a thick plate having maximum and minimum dimensions of 0.15 and 0.30 mm, was described by nine planes. It was necessary to use an estimate for the mass absorption coefficient of Am; a value of 60 cm^2 g^{-1} was extrapolated from the known values for U and Pu.[8] Linear absorption coefficients are 32.4 and 42.7 cm^{-1} for the Eu- and Am-containing compounds, respectively. Calculated transmission factors for the two crystals were in the range 0.55–0.65.

The intensities were corrected for absorption and reduced to structure-factor amplitudes on an absolute scale (see Tables I and II). The three-dimensional Patterson function calculated from the CsEu(HFA)$_4$ data was used to locate Cs and Eu atoms; the positions of the other atoms (excluding H) were obtained from a succession of difference Fourier maps. Refinement of the positions of the 28 independent atoms, each with anisotropic thermal parameters, was carried out by the iterative full-matrix least-squares method using a modified version of the program ORFLS.[9] Each observation was weighted as the reciprocal of its variance, which was estimated as described previously.[10] For CsAm(HFA)$_4$ the light atoms were less well determined, and it was necessary to constrain the thermal motion of the C atoms to be isotropic. The refined parameters of both structures are listed in Table III. Conventional R indices were 0.085 and 0.06 for CsEu(HFA)$_4$ and CsAm(HFA)$_4$, respectively.

Results and Discussion

The orthorhombic unit cells have the following dimensions at 23° based on λ 0.70926 Å for Mo Kα_1: for CsEu(HFA)$_4$, a = 8.660 (4) Å, b = 21.75 (2) Å, and c = 17.43 (2) Å; for CsAm(HFA)$_4$, a = 8.62 (2) Å, b = 21.93 (6) Å, and c = 17.45 (5) Å. The space group indicated by systematic absences and confirmed by the structure determination is Pbcn.

It is seen that there are significant differences between the entries of Table III and the corresponding parameters for CsY(HFA)$_4$ as well as between the two compounds of the table; but these are to be expected from, among other things, the presence of different metal ions in the three compounds. The differences[11] in the trivalent metal radii are reflected, for example, in the average bond length of 2.41 Å found for Am–O compared to 2.38 Å for Eu–O and 2.32 Å for Y–O. Nevertheless, the compounds are clearly isomorphous and exhibit the same qualitative features of symmetry and packing previously described,[5] namely, that the chelate ligands are essentially planar but folded along the O···O line by about 8° with respect to the O–M–O plane, that the type of span by the ligands and the dodecahedron of O atoms results in approximately D$_2$ symmetry for the anions, and that the terminal F atoms execute large thermal motions with anisotropies indicative of large oscillations of the CF$_3$ groups. Bennett, *et al.*,[5] stated that for CsY(HFA)$_4$, Laue photographs indicated variable amounts of disorder in different samples but they did not describe how this disorder was reflected in the films. Our precession photographs of CsEu(HFA)$_4$ and CsAm(HFA)$_4$ appeared normal; the only suggestion of disorder is in the large amplitudes of thermal motion of the CF$_3$ groups.

A comparison of the bond distances and angles among the three compounds is given in Figure 1. These distances are uncorrected for thermal motion, although a correction would be appreciable in the C–F

---

[7] D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, a Fortran Program for Calculating Single-Crystal Absorption Corrections," Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[8] R. B. Roof, *Phys. Rev.*, **113**, 820 (1959).

[9] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[10] J. H. Burns, R. D. Ellison, and H. A. Levy, *Acta Cryst.*, **B24**, 230 (1968).

[11] Although the significance of the difference between the first two bond lengths is doubtful, the expected trend is seen when all three are considered.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CsAm(HFA)$_4$ ON AN ABSOLUTE SCALE[a]

L	OBS	CAL	L	OBS	CAL	L	OBS	CAL	L	OBS	CAL
**0	0	L**	4	61	60	5	9	10	11	155	146
4	0	43	5	131	125	6	62	64	**1	8	L**
6	271	283	6	55	52	7	22	5	1	14	9
8	260	268	7	71	64	8	0	9	2	37	39
10	264	264	8	81	71	9	20	6	3	89	88
12	201	204	9	27	32	10	31	34	4	22	31
14	143	137	10	46	45	11	19	6	5	89	90
**0	2	L**	11	50	57	12	29	20	6	51	53
3	299	294	12	47	47	**1	3	L**	7	13	13
4	500	503	**0	12	L**	0	114	113	8	31	23
5	137	139	2	86	88	1	0	6	9	16	13
6	265	274	3	115	108	2	254	252	10	20	9
7	137	138	4	79	78	3	138	129	11	22	35
8	287	266	5	130	128	4	310	306	**1	9	L**
9	190	185	6	36	25	5	67	69	0	272	259
10	152	156	7	95	97	6	145	156	1	368	350
11	150	145	8	74	66	7	35	31	2	254	251
12	153	146	9	63	62	8	129	121	3	204	208
13	90	94	10	29	30	9	32	36	4	224	227
14	103	100	11	60	62	10	149	151	5	221	219
**0	4	L**	**0	14	L**	11	0	23	6	199	199
0	161	163	0	155	153	12	122	125	7	191	190
1	205	191	1	38	25	**1	4	L**	8	172	177
2	0	16	2	132	135	1	38	38	9	135	139
3	592	568	3	22	8	2	304	305	10	107	107
4	134	137	4	158	158	3	113	113	11	138	137
5	378	386	5	31	11	4	20	14	12	82	68
6	145	149	6	153	152	5	11	19	**1	10	L**
7	285	274	7	26	18	6	23	32	1	0	30
8	83	85	8	114	116	7	68	65	2	52	45
9	187	186	9	0	7	8	0	14	3	0	1
10	48	55	**0	16	L**	9	14	8	4	47	54
11	179	171	0	82	83	10	40	27	5	9	10
12	12	33	1	112	104	11	34	32	6	0	2
13	152	148	2	120	122	12	32	19	7	0	4
14	0	3	3	113	114	**1	5	L**	8	24	11
**0	6	L**	4	121	119	0	245	246	9	15	10
0	0	23	5	65	58	1	273	265	10	17	24
1	257	248	6	123	117	2	109	110	11	13	17
2	67	71	7	54	64	3	229	230	12	22	19
3	247	250	**0	18	L**	4	140	140	**1	11	L**
4	105	105	0	32	17	5	310	309	0	268	264
5	257	254	1	134	139	6	191	183	1	62	59
6	123	126	2	34	29	7	173	186	2	324	313
7	273	277	3	132	138	8	115	125	3	48	51
8	98	84	**1	0	L**	9	129	119	4	336	326
9	231	221	2	58	56	10	114	103	5	73	67
10	68	78	4	208	202	11	153	148	6	248	240
11	127	140	6	10	13	**1	6	L**	7	32	26
12	72	64	8	29	17	1	67	68	8	183	176
13	68	58	10	25	16	2	62	62	9	28	32
14	50	60	12	23	23	3	0	4	10	150	149
**0	8	L**	14	0	17	4	39	37	11	38	38
0	77	77	**1	1	L**	5	38	48	**1	12	L**
1	67	69	0	143	130	6	10	11	1	31	31
2	143	138	1	185	164	7	0	9	2	0	5
3	55	54	2	111	108	8	0	15	3	28	29
4	152	152	3	130	186	9	37	21	4	0	6
5	31	37	4	82	87	10	25	23	5	13	20
6	166	175	5	25	33	11	35	9	6	0	8
7	29	16	6	68	73	**1	7	L**	7	37	46
8	183	175	7	84	83	0	97	99	8	0	6
9	106	99	8	75	74	1	320	337	9	26	4
10	119	118	9	99	98	2	57	58	10	21	0
11	39	45	10	63	68	3	322	328	11	13	20
12	66	61	11	58	54	4	57	65	**1	13	L**
13	5	14	12	53	44	5	307	304	0	231	232
**0	10	L**	**1	2	L**	6	16	16	1	138	137
0	13	25	1	28	30	7	308	316	2	224	213
1	120	119	2	12	7	8	0	13	3	113	101
2	125	124	3	96	100	9	247	251	4	225	217
3	143	131	4	100	91	10	21	3	5	114	112

L	OBS	CAL	L	OBS	CAL	L	OBS	CAL	L	OBS	CAL
6	195	185	3	189	193	**2	7	L**	5	73	78
7	91	91	4	274	298	1	11	15	6	72	72
8	140	135	5	217	219	2	85	80	7	64	69
9	57	49	6	352	353	3	40	45	8	37	34
10	106	110	7	175	171	4	75	79	9	51	48
**1	14	L**	8	219	225	5	11	1	10	39	35
1	21	7	9	158	160	6	36	34	**2	13	L**
2	0	0	10	184	179	7	59	64	1	0	2
3	0	14	11	131	130	8	16	13	2	13	7
4	0	19	12	132	129	9	31	12	3	16	4
5	0	5	13	89	84	10	0	20	4	0	6
6	0	29	14	102	100	11	18	6	5	10	15
7	0	15	**2	3	L**	12	12	3	6	0	2
8	0	6	1	45	43	13	23	2	7	0	1
9	7	6	2	48	49	**2	8	L**	8	0	4
**1	15	L**	3	39	38	0	333	334	9	0	15
0	59	47	4	0	16	1	92	91	**2	14	L**
1	184	181	5	63	51	2	195	190	0	211	187
2	76	72	6	13	14	3	31	32	1	23	19
3	161	153	7	79	58	4	105	108	2	170	164
4	52	59	8	31	25	5	83	81	3	2	7
5	131	131	9	37	41	6	105	108	4	120	121
6	57	57	10	29	10	7	24	22	5	0	11
7	141	136	11	21	17	8	102	101	6	109	111
8	58	58	12	21	18	9	38	35	7	22	14
**1	16	L**	13	0	1	10	96	101	8	89	90
1	0	0	14	19	7	11	0	2	**2	15	L**
2	0	2	**2	4	L**	12	83	89	1	19	20
3	0	25	0	114	124	**2	9	L**	2	28	26
4	0	21	1	257	270	1	0	5	3	0	11
5	0	31	2	172	170	2	90	89	4	26	29
6	0	12	3	314	327	3	10	4	5	32	21
7	0	6	4	91	89	4	61	63	6	15	27
**1	17	L**	5	394	396	5	18	20	7	5	17
0	59	53	6	115	110	6	20	19	**2	16	L**
1	104	100	7	280	269	7	14	20	0	155	161
2	59	58	8	52	47	8	0	2	1	99	101
3	97	100	9	214	216	9	0	13	2	115	123
4	39	45	10	41	48	10	0	6	3	117	117
5	110	110	11	169	165	11	27	16	4	100	91
**1	18	L**	12	24	29	12	0	8	5	96	91
1	3	12	13	103	104	**2	10	L**	6	96	93
2	0	23	**2	5	L**	0	44	42	**2	17	L**
3	0	8	1	20	21	1	73	74	1	0	6
**2	0	L**	2	29	35	2	89	88	2	0	0
0	405	384	3	37	37	3	91	91	3	0	22
2	535	509	4	15	4	4	111	111	4	0	16
4	292	310	5	0	10	5	125	118	**3	0	L**
6	467	473	6	0	9	6	18	13	2	86	79
8	318	333	7	63	33	7	54	54	4	58	57
10	240	229	8	15	21	8	47	43	6	6	30
12	181	171	9	26	20	9	61	68	8	14	18
14	142	135	10	27	4	10	32	28	10	23	17
**2	1	L**	11	0	17	11	55	62	12	0	20
1	28	26	12	15	25	**2	11	L**	**3	1	L**
2	193	199	13	0	11	1	3	2	0	50	43
3	36	31	**2	6	L**	2	40	26	1	21	19
4	25	24	0	43	46	3	13	9	2	99	98
5	46	59	1	197	197	4	24	26	3	83	85
6	51	32	2	75	77	5	12	1	4	131	131
7	61	63	3	323	333	6	28	20	5	176	180
8	34	14	4	88	94	7	0	2	6	97	100
9	0	15	5	170	176	8	0	1	7	84	77
10	28	28	6	121	124	9	0	3	8	86	82
11	26	13	7	156	147	10	30	17	9	100	95
12	13	5	8	143	142	11	0	5	10	58	45
13	0	4	9	147	148	**2	12	L**	11	61	63
14	19	6	10	55	52	0	49	49	12	46	38
**2	2	L**	11	110	113	1	116	115	13	69	51
0	258	259	12	65	47	2	85	80	**3	2	L**
1	378	377	13	76	75	3	154	155	1	40	33
2	415	418				4	93	87	2	55	55

L	OBS	CAL	L	OBS	CAL	L	OBS	CAL	L	OBS	CAL
3	80	75	4	58	62	4	170	169	**4	4	L**
4	69	66	5	221	222	5	70	73	0	15	11
5	134	128	6	13	12	6	151	152	1	312	295
6	21	1	7	231	221	7	84	87	2	48	48
7	62	58	8	12	28	8	125	125	3	269	265
8	23	12	9	195	185	**3	14	L**	4	130	137
9	33	37	10	39	39	1	0	13	5	248	262
10	0	9	11	143	135	2	24	21	6	65	68
11	17	6	12	18	15	3	23	21	7	214	217
12	30	3	**3	8	L**	4	0	7	8	63	59
13	0	4	1	54	43	5	11	20	9	132	147
**3	3	L**	2	65	64	6	0	10	10	49	51
0	155	151	3	29	18	7	13	1	11	116	114
1	37	42	4	24	4	**3	15	L**	**4	5	L**
2	234	234	5	2	0	0	44	41	1	28	34
3	105	116	6	0	8	1	166	159	2	30	32
4	198	197	7	23	9	2	43	46	3	35	33
5	0	4	8	23	21	3	147	146	4	23	19
6	154	157	9	37	31	4	41	40	5	12	24
7	29	22	10	13	11	5	130	131	6	27	25
8	148	138	11	34	11	6	0	28	7	22	25
9	34	30	**3	9	L**	**3	16	L**	8	27	35
10	120	111	0	184	181	1	0	9	9	3	5
11	9	16	1	238	231	2	13	15	10	26	14
12	80	90	2	210	206	3	0	11	11	15	7
13	0	1	3	175	184	4	3	20	**4	6	L**
**3	4	L**	4	163	169	**4	0	L**	0	139	134
1	98	102	5	185	205	6	273	272	1	214	211
2	75	75	6	145	151	8	232	244	2	95	97
3	25	27	7	189	184	10	202	197	3	198	203
4	128	121	8	149	150	12	182	174	4	77	80
5	0	5	9	135	134	**4	1	L**	5	170	180
6	34	27	10	141	148	1	44	43	6	79	82
7	27	25	11	113	104	2	77	76	7	121	126
8	31	31	**3	10	L**	3	26	0	8	43	41
9	21	11	1	27	33	4	28	3	9	114	111
10	41	44	2	1	7	5	37	38	10	41	39
11	23	10	3	6	3	6	0	19	11	95	100
12	27	1	4	10	6	7	11	12	**4	7	L**
13	0	1	5	16	20	8	10	1	1	0	10
**3	5	L**	6	21	3	9	17	2	2	11	21
0	84	83	7	1	16	10	0	9	3	2	10
1	348	335	8	13	1	11	0	11	4	27	34
2	159	160	9	0	5	12	25	1	5	23	11
3	160	165	10	26	6	**4	2	L**	6	10	6
4	161	165	**3	11	L**	0	223	209	7	18	11
5	196	200	0	295	302	1	311	285	8	11	3
6	122	128	1	37	40	2	245	245	9	8	11
7	174	179	2	280	285	3	210	206	10	16	4
8	97	97	3	84	81	4	332	320	11	30	10
9	127	128	4	232	232	5	125	130	**4	8	L**
10	81	74	5	25	27	6	228	229	0	114	118
11	97	93	6	194	200	7	119	122	1	28	26
12	61	67	7	43	27	8	222	222	2	132	138
**3	6	L**	8	174	178	9	107	115	3	41	43
1	56	50	9	0	17	10	124	119	4	126	125
2	52	50	10	155	164	11	112	105	5	39	36
3	18	16	**3	12	L**	12	118	106	6	119	122
4	20	4	1	10	4	**4	3	L**	7	40	42
5	26	26	2	0	14	1	93	88	8	100	102
6	14	10	3	0	11	2	23	13	9	0	19
7	17	25	4	0	8	3	84	86	10	76	85
8	25	29	5	0	11	4	43	48	**4	9	L**
9	19	21	6	0	4	5	31	24	1	33	35
10	33	20	7	32	26	6	13	11	2	44	45
11	30	26	8	4	5	7	15	16	3	5	11
12	19	21	9	0	13	8	0	2	4	21	15
**3	7	L**	**3	13	L**	9	22	21	5	0	17
0	109	101	0	207	212	10	18	19	6	19	7
1	388	389	1	116	116	11	0	1	7	21	19
2	20	19	2	162	185	12	11	1	8	0	4
3	294	309	3	92	85				9	0	7

L	OBS	CAL	L	OBS	CAL	L	OBS	CAL	L	OBS	CAL
10	21	10	6	26	26	1	170	170	2	99	96
**4	10	L**	7	0	3	2	148	148	3	182	181
0	48	51	8	19	24	3	154	156	4	51	45
1	81	80	9	0	3	4	135	139	5	180	175
2	58	57	10	22	11	5	144	150	6	10	4
3	78	78	**5	3	L**	6	115	122	7	146	153
4	50	49	0	157	153	7	152	162	**6	5	L**
5	59	56	1	31	30	8	104	109	1	29	21
6	66	67	2	171	165	**5	10	L**	2	10	3
7	58	60	3	24	26	1	24	0	3	26	29
8	37	47	4	168	169	2	0	11	4	0	11
9	71	92	5	38	43	3	34	10	5	31	36
**4	11	L**	6	103	100	4	0	11	6	24	9
1	12	21	7	28	31	5	29	24	7	13	5
2	30	28	8	113	111	6	19	28	**6	6	L**
3	18	22	9	30	31	7	0	5	0	68	73
4	40	34	10	88	93	**5	11	L**	1	184	173
5	21	6	**5	4	L**	0	183	189	2	52	42
6	13	7	1	0	11	1	10	19	3	136	139
7	7	8	2	17	16	2	192	194	4	73	74
8	27	32	3	24	35	3	42	39	5	94	89
**4	12	L**	4	16	22	4	180	187	6	73	76
0	32	38	5	25	21	5	57	60	**6	7	L**
1	57	57	6	0	32	6	159	171	1	0	15
2	68	67	7	24	19	**5	12	L**	2	4	7
3	76	82	8	17	22	1	0	17	3	19	22
4	61	59	9	0	7	2	13	5	4	27	4
5	87	91	10	25	18	3	24	27	5	25	20
6	32	31	**5	5	L**	4	0	17	6	11	12
7	74	80	0	178	176	5	23	35	**6	8	L**
**4	13	L**	1	179	183	**5	13	L**	0	118	115
1	0	12	2	133	134	0	139	136	1	23	22
2	28	14	3	220	216	1	78	82	2	100	100
3	35	36	4	102	104	2	142	141	3	14	17
4	19	3	5	119	119	3	64	59	4	97	92
5	0	13	6	56	68	**6	0	L**	5	36	31
6	19	5	7	119	126	0	268	248	**6	9	L**
**4	14	L**	8	52	59	2	316	298	1	14	6
0	131	132	9	83	90	4	237	224	2	29	19
1	16	6	10	85	79	6	209	202	3	18	20
2	116	115	**5	6	L**	8	197	200	4	26	10
3	10	15	1	29	30	**6	1	L**	**6	10	L**
4	110	117	2	16	6	1	17	10	0	0	13
5	0	1	3	23	3	2	54	52	1	65	65
**4	15	L**	4	28	29	3	0	3	2	22	30
1	20	1	5	11	7	4	30	35	**7	0	L**
2	0	13	6	34	30	5	18	2	2	72	26
3	11	8	7	19	13	6	26	[illegible]	4	22	14
**5	0	L**	8	19	7	7	28	23	**7	1	L**
2	0	7	9	23	14	8	18	1	0	51	36
4	0	15	**5	7	L**	**6	2	L**	1	72	67
6	17	7	0	15	22	0	232	220	2	47	39
8	24	37	1	243	238	1	133	124	3	43	39
10	0	7	2	34	28	2	220	209	4	31	38
**5	1	L**	3	237	232	3	146	140	**7	2	L**
0	92	88	4	44	40	4	172	173	1	19	11
1	76	73	5	203	210	5	130	121	2	23	11
2	46	37	6	26	8	6	165	163	3	5	10
3	65	64	7	167	174	7	130	138	**7	3	L**
4	95	90	8	0	21	8	129	128	0	100	95
5	76	81	9	144	136	**6	3	L**	1	28	24
6	65	62	**5	8	L**	1	22	10	2	110	105
7	85	83	1	27	2	2	41	39	3	0	14
8	28	35	2	34	33	3	0	7	**7	4	L**
9	48	43	3	15	10	4	22	15	1	0	4
10	52	62	4	23	10	5	34	24	2	37	12
**5	2	L**	5	23	8	6	16	3	**7	5	L**
1	56	50	6	0	31	7	0	17	0	73	80
2	27	15	7	5	16	8	22	3	1	73	68
3	31	21	8	0	13	**6	4	L**			
4	15	19	**5	9	L**	0	72	71			
5	0	2	0	134	192	1	220	213			

[a] The column headings have the same meanings as in Table I.

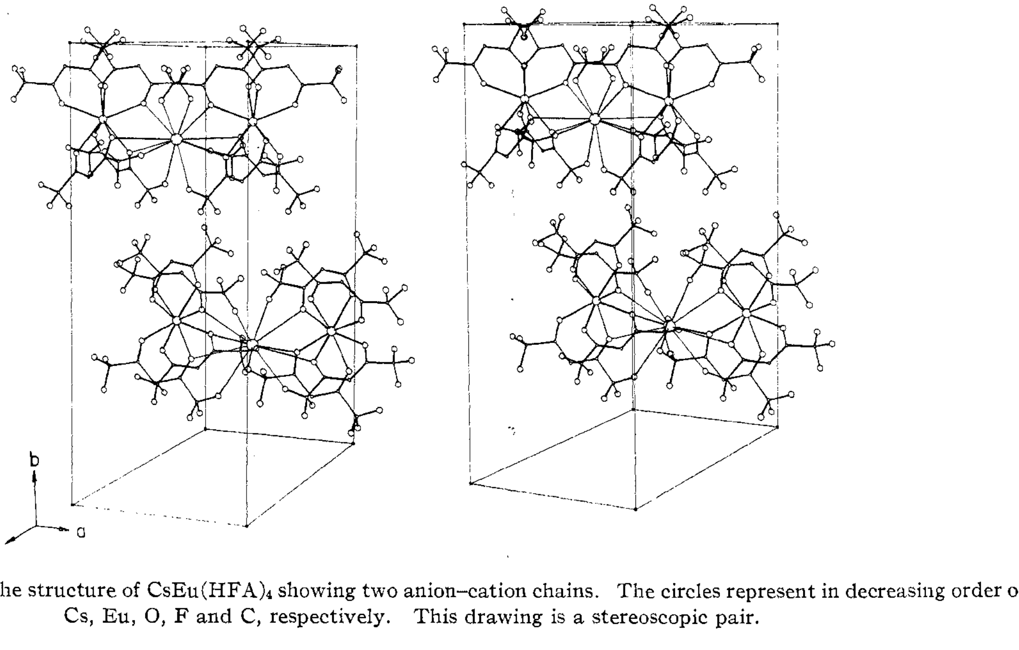


Figure 2.—A portion of the structure of CsEu(HFA)$_4$ showing two anion–cation chains. The circles represent in decreasing order of size Cs, Eu, O, F and C, respectively. This drawing is a stereoscopic pair.

separation. Average standard errors for the distances in the figure are shown in Table IV.

A feature of the structure for which our description differs from that of Bennett, *et al.*,[5] is in the coordination of the Cs$^+$ ion. While they describe it as consisting of eight F atoms in CsY(HFA)$_4$ at pairs of distances of 3.21, 3.27, 3.31, and 3.75 Å, we would rule out the last pair as being too long and instead include six O atoms in pairs at 3.29, 3.40, and 3.50 Å, thus giving the Cs$^+$ in CsY(HFA)$_4$ a 12-fold coordination. In CsEu(HFA)$_4$ the 12 neighbor distances are, in pairs: Cs–F at 3.16, 3.19, 3.30 Å, Cs–O at 3.29, 3.36, 3.48 Å. In CsAm(HFA)$_4$ they are: Cs–F at 3.20, 3.29, 3.34 Å; Cs–O at 3.25, 3.35, 3.46 Å. These contacts are shown in Figure 2, in which a portion of two anion–cation chains is illustrated. The only symmetry exhibited by the

TABLE III

POSITIONAL AND THERMAL PARAMETERS FOR $CsEu(HFA)_4$ (TOP) AND $CsAm(HFA)_4$ (BOTTOM) AND THEIR STANDARD ERRORS[a]

Atom	x	y	z	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cs	0.5(0)[b]	0.26957(7)	0.25(0)	118(2)	41(1)	66(1)	0(0)	2(2)	0(0)
Eu	0.0(0)	0.31651(4)	0.25(0)	89(1)	19(1)	46(1)	0(0)	2(1)	0(0)
O1	-0.221(1)	0.3569(5)	0.3179(6)	93(16)	30(3)	45(5)	-3(7)	18(7)	0(3)
O2	.084(1)	0.4009(6)	0.3246(7)	109(17)	36(4)	62(6)	2(7)	-9(9)	0(4)
O3	-0.139(1)	0.2308(5)	0.3002(7)	127(18)	21(3)	54(5)	7(6)	3(8)	-6(3)
O4	0.152(1)	0.2745(5)	0.3495(6)	194(21)	30(3)	43(5)	-21(7)	-15(9)	12(4)
F1	-0.427(2)	0.4449(9)	0.437(1)	197(22)	106(8)	154(12)	13(11)	60(13)	83(9)
F2	-0.488(2)	0.3671(7)	0.386(2)	259(30)	65(6)	329(25)	82(13)	213(25)	75(11)
F3	-0.481(2)	0.4397(13)	0.331(1)	152(26)	202(16)	140(11)	-121(19)	73(14)	-86(11)
F4	0.220(2)	0.4731(6)	0.438(1)	264(26)	60(5)	107(9)	-15(9)	-53(13)	-30(5)
F5	0.212(2)	0.5139(6)	0.332(1)	502(38)	55(5)	100(9)	-120(12)	74(15)	-13(5)
F6	0.055(1)	0.5385(5)	0.418(1)	194(22)	40(3)	190(12)	0(7)	-3(12)	-48(5)
F7	-0.219(2)	0.1045(10)	0.410(1)	613(55)	108(9)	158(14)	190(19)	-116(22)	-92(11)
F8	-0.194(3)	0.0969(9)	0.299(1)	846(88)	77(7)	186(18)	184(24)	86(28)	55(10)
F9	-0.347(1)	0.1503(7)	0.339(2)	195(26)	37(5)	382(26)	52(9)	-57(23)	-67(9)
F10	0.251(2)	0.2462(14)	0.509(1)	339(35)	201(18)	89(10)	60(17)	-85(18)	-46(10)
F11	0.406(2)	0.2359(9)	0.420(1)	157(22)	148(11)	127(10)	-46(13)	-60(13)	96(9)
F12	0.297(2)	0.1642(7)	0.469(1)	347(31)	65(6)	153(13)	-12(12)	-115(17)	35(8)
C1	-0.409(2)	0.4093(14)	0.386(2)	105(41)	54(10)	131(19)	-60(16)	-54(22)	55(11)
C2	-0.242(2)	0.4050(8)	0.358(1)	157(30)	26(5)	36(7)	-26(10)	37(12)	-4(5)
C3	-0.138(2)	0.4515(7)	0.378(1)	136(30)	18(4)	58(8)	4(10)	-2(13)	-1(5)
C4	0.016(2)	0.4426(8)	0.360(1)	168(37)	26(5)	56(8)	32(16)	-7(19)	1(5)
C5	0.127(2)	0.4952(10)	0.384(1)	191(37)	24(6)	78(13)	-3(14)	19(19)	6(7)
C6	-0.211(3)	0.1347(16)	0.353(2)	256(54)	63(11)	111(19)	92(22)	-45(26)	-4(13)
C7	-0.099(2)	0.1881(9)	0.346(1)	100(32)	28(6)	76(12)	29(13)	28(15)	18(7)
C8	0.032(2)	0.1781(8)	0.391(1)	131(41)	26(4)	64(9)	17(10)	8(13)	-9(6)
C9	0.144(2)	0.2271(8)	0.388(1)	145(30)	34(6)	36(8)	-3(12)	0(13)	1(6)
C10	0.282(4)	0.2215(15)	0.446(2)	357(66)	51(9)	60(12)	21(22)	8(27)	40(10)
Cs	0.5(0)	0.26803(9)	0.25(0)	121(4)	38(1)	63(1)	0(0)	1(3)	0(0)
Am	0.0(0)	0.31633(4)	0.25(0)	88(2)	16(1)	43(1)	0(0)	3(2)	0(0)
O1	-0.227(2)	0.3554(6)	0.3155(8)	105(26)	20(4)	32(7)	2(9)	9(12)	4(5)
O2	0.080(2)	0.3998(7)	0.3255(8)	108(25)	28(4)	49(8)	-5(9)	12(12)	-30(5)
O3	-0.141(2)	0.2294(7)	0.3048(9)	83(28)	33(5)	48(8)	18(9)	-18(12)	-11(6)
O4	0.156(2)	0.2735(7)	0.3512(9)	140(31)	23(5)	45(8)	0(9)	-39(13)	-5(5)
F1	-0.432(2)	0.443(1)	0.435(2)	150(32)	112(11)	138(16)	12(14)	48(18)	77(13)
F2	-0.490(3)	0.367(1)	0.391(2)	318(43)	54(6)	293(30)	51(18)	217(34)	45(12)
F3	-0.484(3)	0.440(2)	0.333(2)	192(39)	236(23)	107(14)	-122(29)	45(25)	-75(15)
F4	0.216(2)	0.476(1)	0.435(1)	250(34)	49(6)	112(13)	-16(11)	-33(20)	-25(7)
F5	0.198(3)	0.515(1)	0.332(1)	588(58)	49(6)	100(12)	-128(17)	79(25)	-23(7)
F6	0.047(2)	0.540(1)	0.419(1)	185(36)	39(5)	167(15)	-16(9)	13(18)	-40(7)
F7	-0.213(3)	0.103(1)	0.406(2)	625(77)	110(12)	167(21)	196(27)	-181(34)	-97(15)
F8	-0.182(4)	0.098(1)	0.302(2)	794(105)	64(9)	180(24)	166(27)	66(39)	33(13)
F9	-0.348(2)	0.149(1)	0.344(3)	225(44)	42(7)	419(40)	37(14)	-68(35)	-68(14)
F10	0.256(3)	0.243(2)	0.504(2)	425(60)	138(13)	116(14)	54(22)	-97(27)	-39(13)
F11	0.414(2)	0.235(1)	0.423(1)	158(30)	130(12)	113(14)	-48(17)	-74(20)	70(11)
F12	0.305(2)	0.161(1)	0.466(2)	307(44)	84(10)	216(24)	-7(17)	-173(28)	64(14)
C1	-0.419(5)	0.411(2)	0.381(3)	8.0(10)[c]					
C2	-0.241(3)	0.405(1)	0.354(2)	4.2(6)					
C3	-0.142(3)	0.449(1)	0.377(2)	4.2(6)					
C4	0.022(3)	0.441(1)	0.359(2)	3.4(5)					
C5	0.113(4)	0.494(2)	0.383(2)	7.5(8)					
C6	-0.225(5)	0.138(2)	0.350(3)	9.1(10)					
C7	-0.096(3)	0.188(1)	0.350(2)	4.9(6)					
C8	0.034(2)	0.177(1)	0.392(1)	4.1(5)					
C9	0.142(3)	0.225(1)	0.392(2)	5.6(7)					
C10	0.285(6)	0.214(2)	0.442(3)	10.2(11)					

a) Coefficients in the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

b) Numbers in parentheses are estimated standard errors for last digit listed.

c) For carbon atoms the coefficients B for isotropic temperature factors are listed.

[a] Numbering scheme is the same as that of Bennett, *et al.*,[5] and agrees with that in Figure 1.

TABLE IV

	M = Y	M = Eu	M = Am
Distance Errors, Å			
M–O	0.01	0.01	0.02
C–O	0.02	0.02	0.03
C–C	0.02	0.02	0.03
C–F	0.03	0.04	0.05
Angle Errors, Deg			
O–M–O	0.3	0.4	0.7
M–O–C	0.7	1.0	1.5
O–C–C	1.0	2.0	2.0
C–C–C	1.0	2.0	3.0

polyhedron consisting of these 12 neighbors is the twofold crystallographic axis passing through the Cs^+ ion. The fact discussed by the previous authors that between chains there are only F···F contacts is also apparent in Figure 2.

CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DEPARTMENT,
CHEMICAL RESEARCH LABORATORY,
EDGEWOOD ARSENAL, MARYLAND 21010

Proton Magnetic Resonance Studies of Phosphoryl Transition Metal Compounds

BY LAWRENCE S. FRANKEL[1]

Received December 4, 1968

The coordination properties of dimethyl methylphosphonate, DMMP = $(CH_3)P(O)(OCH_3)_2$, and trimethyl phosphate,[2] TMP = $(O)P(OCH_3)_3$, have been investigated. The proton spin–spin relaxation times (T_2) and the phosphorus spin-lattice relaxation times (T_1) of compounds of the type $M(L)_X(ClO_4)_2$ (M is an iron series transition metal, L is a phosphoryl ligand, and X is the coordination number) have been examined in neat solutions of the ligands in an effort to study the ligand-exchange reactions.

The hexamethylphosphoramide, HMPA = $(O)P(N(CH_3)_2)_3$, complexes were prepared as previously described.[3] A similar procedure was used to prepare the DMMP and TMP complexes. Dehydration of $M(H_2O)_6(ClO_4)_2$ with triethyl orthoformate was followed by the addition of a slight excess of ligand. The complexes were precipitated, as oils, upon the addition of diethyl ether. Solids were obtained by repeated washing with fresh ether. The solids were dried *in vacuo* over P_2O_5. The compounds isolated are shown in Table I. This procedure did not give pure solids in the following cases: DMMP with Fe^{2+}, Co^{2+}, and Ni^{2+}; TMP with Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}; and dimethyl hydrogen phosphite, DHP = $(H)P(O)(OCH_3)_2$, with the entire iron series.

All solutions were made in a nitrogen atmosphere. The nmr data were obtained on a Varian A-60 spectrometer. The effective magnetic moments were determined by the method of Evans[4] using benzene as an inert reference in a solution of the ligand. Infrared spectra were obtained on a 521 Perkin-Elmer grating spectrometer (Nujol on CsI plates). The concentration of complex used to obtain the relaxation time data was: $Co(HMPA)_4^{2+}$, (0.67–1.6) × 10^{-2} *M;* $Fe(HMPA)_4^{2+}$, (0.45–1.3) × 10^{-2} *M;* $Mn(HMPA)_4^{2+}$, (0.12–3.1) × 10^{-2} *M;* $Mn(DMMP)_6^{2+}$, (0.14–7.2) × 10^{-2}*M;* $Mn(TMP)_6^{2+}$, (2.0–5.3) × 10^{-2} *M*.

The infrared phosphoryl shifts (Table I) clearly show that coordination involves the phosphoryl group. As is typical Fe^{3+} gives a much larger shift than Mn^{2+}. The analytical data are tabulated in Table I as are the effective magnetic moments (μ). HMPA, diisopropyl methylphosphonate,[5] and triphenyl phosphine oxide[6]

---

[1] Rohm and Haas Co., Research Laboratory 13, Philadelphia, Pa. 19137.

[2] V. Gutmann and W. K. Lux, *J. Inorg. Nucl. Chem.*, **29**, 2391 (1967).

[3] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

[4] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[5] N. M. Karayannis, C. Owens, L. L. Pytlewski, and M. M. Labes, submitted for publication.

[6] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).