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The Preparation, Properties, and Structure of Tetraphenylarsonium Tetrakis(trifluoroacetato)cobaltate(II)[1]

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The compound $[(C_6H_5)_4As]_2[Co(O_2CCF_3)_4]$ has been prepared and thoroughly characterized. A single-crystal X-ray diffraction study has shown that the cation has distorted S_4 symmetry and the anion a structure in which the coordination of the Co(II) ion is intermediate between tetrahedral and dodecahedral. Four Co–O bonds of length 2.00 ± 0.03 A define a bisphenoid (tetrahedron distorted to D_{2d} symmetry) with its two equal angles having the value 97 ± 2°, while there are four more oxygen atoms at distances of 3.11 ± 0.03 A from Co defining a very flat bisphenoid (nearly a square) with vertical angles of 163 ± 2°. The visible spectrum and magnetic moment lead to electronic structure parameters in good accord with those for tetrahedral Co(II) complexes generally, and it is concluded that the $Co(O_2CCF_3)_4^{2-}$ ion can be so described for all practical purposes. The structure is compared to that of the more nearly dodecahedral $Co(NO_3)_4^{2-}$ ion.

Introduction

When it had been shown[2] that the $Co(NO_3)_4^{2-}$ ion contained bidentate nitrate ions and thus octacoordinate Co(II), it seemed interesting to investigate the preparation, electronic structure, and perhaps the molecular structure of the corresponding trifluoroacetate complex, provided, of course, that such a complex could be isolated. The CF_3COO^- ion was selected since it is isoelectronic and isostructural with the nitrate ion insofar as the functional portion of the ion is concerned, and it is the anion of a strong acid, though not so strong as nitric acid.

The preparation of $Co(O_2CCF_3)_4^{2-}$ and its isolation as the tetraphenylarsonium salt proved to be quite easy, and it was immediately observed that its electronic spectrum and magnetic properties closely resemble those of $Co(NO_3)_4^{2-}$ (and, of course, also those of ordinary four-coordinate, tetrahedral Co(II) complexes). It therefore seemed worthwhile to carry out a single-crystal X-ray study to establish definitively the structure of the $Co(O_2CCF_3)_4^{2-}$ ion. This paper describes all of the investigations outlined above.

Experimental Section

Preparation.—The complex was prepared by mixing stoichiometric quantities of $(C_6H_5)_4AsCl$, CF_3COOAg, and $CoCl_2$ in acetonitrile. After separating the insoluble silver chloride by decantation, ethyl ether was added dropwise until the solution became cloudy. The solution was then covered and allowed to stand. After approximately 8 hr, the large, well-developed, blue-violet crystals were collected by filtration, washed with ether, and dried under vacuum. *Anal.* Calcd for $C_{56}H_{40}F_{12}As_2O_8Co$: C, 52.64; H, 3.16. Found: C, 52.59; H, 3.32.

Visible Spectrum.—This was measured using a Cary Model 14 recording spectrometer. The results are shown in Figure 4.

Magnetic Susceptibilities.—These were measured using a Gouy balance. The corrected molar susceptibilities (in cgs units × 10^6) at four temperatures were as follows: 77°K, 29,030; 195°K, 12,780; 260°K, 9,770; 300°K, 8,010. Corrections were: for diamagnetism, 645×10^{-6} cgs unit; for temperature-independent paramagnetism, -510×10^{-6} cgs unit. These results correspond to the Curie–Weiss law, $\mu = 2.84\sqrt{X_M^{coor}(T - \theta)}$, with $\mu = 4.55 \pm 0.05$ BM and $\theta = 10°$.

X-Ray Examination, Unit Cell, Space Group.—Precession photographs showed a tetragonal unit cell of dimensions $a = 11.68 \pm 0.01$ A, $c = 40.84 \pm 0.04$ A, $V = 5570$ A^3. The density, measured by flotation, was 1.54 ± 0.05 g cm^{-3} indicating $Z = 4$ (calcd, 1.52 g cm^{-3}). Systematic absences were: for hkl, $h + k + l \neq 2n$; for $hk0$, $h(k) \neq 2n$; for $00l$, $l \neq 4n$. These absences uniquely establish the space group as $I4_1/a$ (no. 88). Intensity data were then collected using a crystal of dimensions ~0.25 mm and Co Kα radiation. Equiinclination levels $h0l$ through $h8l$ were recorded by the multiple-film technique. The intensities of 726 independent reflections, accessible within the angular range $\theta_{Co} \leq 50°$, were estimated visually using a calibration wedge prepared from the same crystal. Absorption corrections (linear absorption coefficient, μ, was 42.5 cm^{-1}) were neglected. Approximately 10% of the reflections were too weak to be measured and were assigned one-half of the minimum observed value in subsequent calculations. Lorentz and polarization corrections were carried out with the program DFSET-4.[3] Electron density summations and Patterson functions were computed using the Fourier program ERFR-2.[4] The structure was refined by the full-matrix, least-squares refinement program of Prewitt,[5] in which the function minimized is $\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2$, where F_o and F_c are the observed and calculated structure factors, respectively, and w is the weighting factor. Equal weights were used until the value of the residual, R, defined as $\Sigma w||F_o| - |F_c||/\Sigma w|F_o|$, dropped to 0.14, after which a weighting scheme was introduced. With the $|F_o|$ on the scale of Table I, in which the final F_c and $|F_o|$ are compared, the weighting scheme had the form $F_o < 40$, $w = 1.4(F_o/100)$; $40 \leq F_o < 180$, $w = 0.32(F_o/100) + 0.43$; $F_o < 180$, $w = 1.0$. Atomic scattering factors for the neutral atoms, tabulated by Ibers,[6] were used.

Determination of Structure

Since the positions of the heavy metal atoms were almost completely fixed by symmetry, *i.e.*, Co $[(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, \frac{1}{4}, \frac{1}{8})]$; As $[(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (0, \frac{1}{4}, z;\ 0, \frac{1}{4}, \frac{1}{4} - z)]$, a three-dimensional Patterson synthesis readily revealed the z coordinate of the arsenic. A three-dimensional Fourier synthesis of the electron density with phases based on the heavy metals revealed plausible locations for 12 of the 14 crystallographically independent carbon atoms as well as

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[1] Supported by grants from the Army Research Office and the National Science Foundation.

[2] J. G. Bergman, Jr., and F. A. Cotton, *Inorg. Chem.*, **5**, 1208 (1966).

[3] D. P. Shoemaker, "An IBM 709/7090 Program for Computing Diffractometer Settings," DFSET-4.

[4] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090," ERFR-2.

[5] C. T. Prewitt, "A Full-Matrix Crystallographic Least-Squares Program for the IBM 709/7090," 1962.

[6] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

TABLE I

OBSERVED[a] AND CALCULATED STRUCTURE FACTORS (×29.85) FOR $[(C_6H_5)_4As]_2[Co(CF_3COO)_4]$

H	L	FOBS	FCAL
****K =		0******	
0	8	2276	-2001
0	12	1914	-1867
0	16	1483	-1337
0	20	1611	-1684
0	24	2187	2025
0	28	1284	1340
0	32	2139	2001
1	3	1741	-1414
1	5	5161	-4955
1	7	1376	1489
1	9	702	522
1	11	1818	-1854
1	13	1372	1004
1	15	2806	2562
1	17	697	276
*1	19	354	-134
1	21	526	305
1	23	492	-21
1	25	1397	1502
1	29	1235	-935
2	0	5707	6730
2	2	1109	1050
2	4	1231	927
2	6	7623	-7999
2	8	836	916
2	10	238	-220
2	12	2368	-2212
2	14	745	-424
2	16	2235	-1880
2	18	867	222
2	20	1950	-1753
*2	22	381	179
2	24	1486	1245
2	26	746	-765
2	28	1034	1071
*2	30	451	664
2	32	2303	2025
3	1	1370	1425
3	3	2882	-2911
3	5	1672	-1322
3	7	248	882
3	9	632	455
3	11	3694	3396
3	13	1976	-1908
3	15	2647	2377
3	17	2631	2458
3	19	1957	-1967
3	21	1031	1153
3	23	944	626
3	25	500	235
3	27	1885	-1694
3	29	1661	-1434
*3	31	459	-255
3	33	858	-822
4	0	4635	4961
*4	2	274	-180
*4	4	279	98
4	6	2983	-2517
4	8	2774	2645
4	10	343	276
4	12	6731	-6124
*4	14	297	220
4	16	2311	-1945
4	18	744	-345
4	20	733	-363
*4	22	376	69
4	24	1686	1494
4	26	793	-809
4	28	1459	1315
*4	30	474	101
4	32	1459	1574
5	1	469	476
5	3	968	-869
5	5	3021	-3206
5	7	2582	2548
*5	9	315	-11
5	11	2601	1897
5	13	652	553
5	15	750	656
5	17	1209	1339
5	19	575	-413
5	21	897	804
*5	23	469	498
*5	25	482	124
5	27	1146	-1144
5	29	872	-798
6	0	3230	3013
6	2	652	468
6	4	949	691
6	6	848	1095
6	8	543	297
6	10	307	154
6	12	1852	-1579
6	14	1067	-1011
6	16	1459	-1206
*6	18	436	-8
6	20	1167	-1088
6	22	456	399
6	24	778	534
6	26	458	-525
6	28	1107	1188
7	1	520	-661
7	3	732	-586
7	5	2627	-2804
7	7	1050	1114
*7	9	372	259
7	11	1312	825
7	13	437	-398
7	15	1138	1224
7	17	842	712
*7	19	457	-125
7	21	779	811
*7	23	457	-353
7	25	581	679
7	27	973	-983
8	0	3565	3607
*8	2	439	202
8	4	442	239
*8	6	444	89
*8	8	447	75
*8	10	451	91
8	12	1669	-1544
*8	14	458	194
8	16	857	-1207
*8	18	458	297
8	20	641	-484
*8	22	444	-451
9	1	1144	-1261
9	3	691	-771
9	5	1990	-1702
9	7	1049	1267
*9	9	459	-243
9	11	710	784
10	0	1949	2097
****K =		1******	
0	27	1366	-1482
*0	31	448	242
1	2	3041	-2959
1	4	408	-265
1	6	1860	-1896
1	8	639	537
1	10	5104	-4898
1	12	1585	1467
1	14	291	-174
1	18	1817	1876
1	20	268	-198
1	22	1856	2009
*1	24	393	-185
*1	26	414	-19
*1	28	433	163
1	30	689	746
1	32	449	58
1	34	1563	-1972
2	1	2109	2464
2	3	1142	-1061
2	5	5957	5804
2	7	2801	2869
2	9	1009	884
2	11	1359	-741
2	13	1471	-1466
2	15	613	556
2	17	1669	-2055
2	19	366	134
2	21	941	-987
2	23	1938	-1967
2	25	824	-668
2	27	1513	-1485
2	29	864	1155
*2	31	449	-248
*2	33	446	773
3	2	4676	-4740
3	4	815	565
3	6	3826	-3720
3	8	1452	1305
3	10	2792	-2882
3	12	1139	857
3	14	1207	1275
3	16	755	621
*3	18	351	173
3	20	397	334
3	22	2998	3098
3	24	740	-640
3	26	730	579
3	28	810	830
*4	1	269	-298
4	3	1912	-2104
4	5	3622	3453
4	7	3379	3451
4	9	2083	1857
4	11	629	-807
4	13	1039	1094
4	15	1126	1032
4	17	682	-793
4	19	410	-307
*4	21	404	-353
*4	23	421	-236
4	25	1175	-1270
4	27	1583	-1611
4	29	779	676
5	2	2097	-2233
5	4	595	-664
5	6	2689	-2480
5	8	1043	897
5	10	3828	-3793
*5	12	356	276
*5	14	371	-11
5	16	719	-667
*5	18	403	384
*5	20	416	182
5	22	2122	2052
*5	24	442	-352
5	26	956	1189
6	1	1149	909
6	3	1529	-1520
6	5	1197	1557
6	7	1028	1549
6	9	986	875
*6	11	386	481
6	13	616	-532
6	15	694	699
6	17	1891	-1810
6	19	461	-223
*6	21	442	-10
6	23	1105	-1089
*6	25	449	-544
6	27	1266	-1329
7	2	2030	-2188
*7	4	399	141
7	6	1905	-1332
7	8	334	316
7	10	2012	-2217
*7	12	425	-190
*7	14	432	310
7	16	520	497
7	18	575	800
*7	20	449	-211
7	22	1735	1817
*8	1	430	286
8	3	731	-708
8	5	1880	1918
8	7	1340	1362
8	9	469	72
8	11	1113	1009
8	13	447	-47
8	15	532	388
8	17	696	-636
9	2	1378	-1625
*9	4	449	156
9	6	636	-480
*9	8	449	-107
9	10	1004	-1094
10	1	519	727
10	3	465	-117
10	5	893	1214
****K =		2******	
1	1	3150	2896
1	3	576	712
1	5	5445	5179
1	7	2489	-2741
*1	9	293	-97
1	11	3826	-3980
1	13	1748	-1951
1	15	1433	-1317
1	17	1851	-1824
1	19	375	370
1	21	940	-949
1	23	1301	1558
1	25	759	-644
1	27	1399	1324
1	29	1191	1413
2	0	5054	4250
2	2	761	-650
2	4	1805	-1763
2	6	2260	-2195
*2	8	256	-86
2	10	757	548
2	12	1537	1319
2	14	356	233
2	16	1395	1453
2	18	725	-674
2	20	2152	2314
2	22	323	251
2	24	900	-829
2	26	514	503
2	28	640	-905
2	30	376	-128
2	32	1532	-1522
3	1	1786	2003
3	3	1418	1175
3	5	3564	3698
3	7	1699	-1814
*3	9	228	-38
3	11	3569	-3588
3	13	842	796
3	15	2417	-2418
3	17	1696	-2005
3	19	1385	1218
3	21	1165	-1234
3	23	343	340
3	25	472	-424
3	27	1209	1185
3	29	992	1028
4	0	1335	-1606
*4	2	231	-58
4	4	1082	-863
4	6	1239	1170
4	8	252	42
4	10	287	11
4	12	4225	4529
4	14	860	-968
4	16	739	874
4	18	523	376
4	20	1293	1332
4	22	665	544
4	24	796	-847
*4	26	372	175
4	28	887	-1115
*4	30	374	246
4	32	1103	-1146
5	1	1312	1456
5	3	269	273
5	5	1353	1299
5	7	2455	-2415
5	9	316	370
5	11	2245	-2251
*5	13	310	-386
5	15	1229	-1271
5	17	1374	-1204
5	19	382	390
5	21	474	-597
5	23	891	833
*5	25	375	-140
5	27	1164	1166
5	29	847	479
6	0	2911	-3136
6	2	399	-273
6	4	1237	-1151
*6	6	310	121
*6	8	317	412
6	10	616	564
6	12	1647	1625
*6	14	343	-202
6	16	990	1207
*6	18	362	33
6	20	1107	1202
*6	22	375	-261
6	24	949	-940
*6	26	373	-139
6	28	936	-1072
7	1	787	772
7	3	1052	925
7	5	1237	1268
7	7	1413	-1358
7	9	350	343
7	11	470	-528
*7	13	362	136
7	15	1098	-1097
7	17	1273	-1249
8	0	2741	-3161
8	2	297	434
8	4	974	-1009
8	6	403	-363
8	8	406	-181
8	10	537	-450
8	12	1227	1292
8	14	377	-414
8	16	1020	1118
*8	18	374	-60
8	20	639	755
8	22	359	444
9	1	1269	1386
9	3	413	470
9	5	1318	1534
9	7	350	-600
9	9	375	200
9	11	374	-420
9	13	370	-647
9	15	581	-562
9	17	846	-894
10	0	1161	-1283
10	2	297	13
****K =		3******	
1	2	1931	2125
1	4	163	325
*1	6	108	348
1	8	586	499
1	10	2186	2359
1	12	947	-828
1	14	413	-116
1	16	310	475
1	18	527	-288
1	20	814	790
1	22	2670	-2866
1	24	371	-411
1	26	1209	-1529
1	28	631	590
*1	30	256	27
1	32	765	899
1	34	1070	1182
2	1	2303	-2172
2	3	1320	1206
2	5	954	753
2	7	1526	-1651
2	9	327	266
2	11	3657	-3376
*2	13	167	-233
2	15	1612	-1817
2	17	4562	4498
2	19	1347	1333
2	21	907	835
2	23	1579	1603
*2	25	242	-205
2	27	2046	1907
2	29	1158	-907
*2	31	256	-17
2	33	900	-959
3	2	1394	1298
3	4	323	-101
3	6	846	493
3	8	513	389
3	10	3568	3325
3	12	764	603
3	14	1336	-1186
3	16	940	-888
3	18	633	-676
*3	20	222	253
3	22	2506	-2533
*3	24	243	-145
3	26	827	-939
*3	28	256	269
*3	30	256	-162
3	32	522	396
4	1	644	-469
4	3	341	-294
4	5	2679	-2729
4	7	1673	-1601
4	9	313	436
4	11	2637	-2685
*4	13	198	157
4	15	2410	-2325
4	17	2530	2552
4	19	901	823
*4	21	239	271
*4	23	247	516
4	25	527	408
4	27	1393	1438
4	29	765	-580
5	2	563	378
5	4	684	551
5	6	771	835
5	8	499	649
5	10	3003	2876
5	12	486	357
*5	14	221	59
*5	16	229	-215
5	18	938	-861
*5	20	245	-433
5	22	1876	-1884
*5	24	255	139
5	26	1160	-1310
6	1	1893	-1956
*6	3	213	-266
6	5	1224	-1391
6	7	789	-781
6	9	388	634
6	11	1038	-1501
6	13	589	701
6	15	1801	-1866
6	17	2018	1766
*6	19	252	268
6	21	442	631
6	23	584	387
6	25	404	584
6	27	1229	1268
7	2	1470	1431
*7	4	236	181
7	6	1493	1657
7	8	384	181
7	10	1667	1592
7	12	566	654
*7	14	251	-380
*7	16	254	31
*7	18	256	-266
*7	20	256	-162
7	22	1573	-1520
8	1	990	-1071
*8	3	251	87
8	5	1719	-1784
8	7	1257	-1285
8	9	442	374
8	11	1158	-1294
8	13	369	-101
8	15	583	-739
8	17	913	1035
*8	19	250	127
8	21	960	1319
9	2	1105	1007
9	4	443	-438
9	6	839	831
*9	8	254	437
9	10	377	781
****K =		4******	
1	1	851	-1049
1	3	598	-1180
1	5	1078	-925
1	7	2921	2977
1	9	958	-769
1	11	394	165
1	13	653	-955
1	15	2134	1910
1	17	2302	2200
*1	19	248	-225
1	21	1021	1094
1	23	699	-975
1	25	662	656
1	27	1827	-1824
1	29	799	-738
2	0	4212	4279
2	2	635	534
2	4	793	956
2	6	2148	1770
2	8	1057	1112
2	10	433	360
2	12	3379	-3417
2	14	762	-811
2	16	1644	-1753
*2	18	350	201
2	20	1657	-1634
*2	22	362	222
2	24	1706	1714
*2	26	299	49
2	28	821	1089
*2	30	304	142
2	32	779	519
3	1	1079	-694
3	3	655	-704
3	5	2927	-2452
3	7	1348	1144
3	9	401	-145
3	11	958	-873
3	13	727	-732
3	15	2604	2554
3	17	3758	3623
3	19	653	-592
3	21	1120	1222
3	23	544	-710
3	25	769	687
3	27	1370	-1483
4	0	2328	3030
*4	2	202	-246
*4	4	206	-70
4	6	696	-539
4	8	493	501
4	10	563	421
4	12	3394	-3116
4	14	328	-147
4	16	1696	-1495
4	18	515	-405
4	20	2114	-2340
*4	22	295	-189
4	24	1214	1234
*4	26	305	236
4	28	946	1123
4	30	295	-84
*5	1	231	125
*5	3	233	64
5	5	1307	-1592
5	7	809	894
*5	9	250	-296
5	11	484	217
5	13	500	661
5	15	1783	1565
5	17	2262	2279
5	19	892	-976
5	21	736	898
5	23	1614	-1579
5	25	518	429
5	27	947	-862
6	0	2291	2229
6	2	636	489
6	4	590	447
6	6	189	-93
6	8	299	219
6	10	393	-607
6	12	2149	-2206
*6	14	291	125
6	16	1259	-1228
*6	18	301	-207
6	20	1326	-1196
6	22	744	692
6	24	824	762
6	26	453	610
*7	1	287	-92
7	3	847	-744
7	5	1642	-1834
7	7	1200	1226
7	9	660	-563
7	11	507	502
7	13	674	601
7	15	568	581
7	17	1624	1924
7	19	470	-594
*7	21	299	139
7	23	546	-799
8	0	1897	1936
*8	2	302	92
8	4	741	621
8	6	622	627
*8	8	304	244
8	10	430	406
8	12	1004	-1068
****K =		5******	
1	2	1282	-1538
1	4	1203	1347
1	6	2361	-2254
*1	8	231	-170
1	10	2827	-2704
1	12	432	161
*1	14	308	-210
1	16	321	146
1	18	410	241
*1	20	378	7
1	22	2149	2236
*1	24	414	69
1	26	776	928
2	1	1417	1541
2	3	901	-642
2	5	1152	1271
2	7	2612	2270
*2	9	268	206
2	11	443	335
2	13	477	-414
2	15	1579	1613
2	17	1843	-1946
2	19	477	-531
2	21	1193	-1287
2	23	753	-642
2	25	536	-333
2	27	655	-772
2	29	492	226
3	2	1421	-1407
3	4	407	524
3	6	1392	-1250
3	8	560	384
3	10	3110	-3025
3	12	499	469
3	14	399	558
3	16	557	-623
3	18	641	770
*3	20	401	-173
3	22	2349	2509
4	1	382	-307
4	3	296	-392
4	5	2814	2745
4	7	1138	1193
4	9	424	53
4	11	337	12
*4	13	365	306
4	15	2029	2028
4	17	1888	-1907
4	19	516	-506
4	21	1808	-1790
4	23	974	-1050
4	25	414	4
5	2	482	-710
*5	4	351	305
5	6	1259	-1276
*5	8	366	-181
5	10	2494	-2357
*5	12	388	150
*5	14	398	311
5	16	473	-291
5	18	1317	1245
*5	20	426	173
5	22	2430	2534
*5	24	426	171
5	26	581	760
6	1	832	649
6	3	490	-603
6	5	1296	1188
6	7	1139	829
6	9	389	4
6	11	784	670
*6	13	416	-16
6	15	1907	1850
6	17	715	-495
6	19	655	-715
6	21	854	-1041
6	23	376	-365
7	2	866	-993
7	4	580	711
7	6	1349	-1275
7	8	408	-153
7	10	2068	-2094
7	12	1025	-983
8	1	495	451
8	3	364	-540
8	5	1081	1438
8	7	1333	1472
*8	9	427	107
8	11	851	1071
*8	13	421	102
8	15	401	399
9	2	527	-620
9	4	372	322
9	6	439	-557
****K =		6******	
1	1	1242	1650
1	3	777	864
1	5	937	1575
1	7	1538	-1489
1	9	262	396
1	11	1173	-1052
1	13	975	-986
1	15	1260	-1003
1	17	1767	-1704
2	0	2739	-3128
*2	2	212	-114
2	4	2461	-2021
*2	6	240	440
2	8	493	-464
*2	10	280	65
2	12	1512	1586
*2	14	323	-556
2	16	1232	1041
*2	18	360	-363
2	20	1240	1083
3	1	2163	2030
3	3	949	976
3	5	1716	1530
3	7	1497	-1273
3	9	479	-487
3	11	1500	-1696
3	13	272	-165
3	15	1659	-1557
4	0	1922	-1987
4	2	913	930
4	4	1113	-956
4	6	549	99
5	1	1233	1128
*5	3	345	137
5	5	1149	946
5	7	1069	-1257
6	0	1944	-2124
*6	2	375	485
6	4	948	-827
****K =		7******	
1	2	1346	1811
1	4	343	482
1	6	1778	1997
*1	8	256	-80
1	10	1463	1567
1	12	771	649
2	1	1637	-1631
2	3	495	467
2	5	1812	-1861
2	7	1075	-761
3	2	2028	1837
3	4	1047	847
3	6	908	808
*3	8	317	-228
3	10	1721	1506
4	1	1074	-826
4	3	571	977
4	5	1742	-1556
5	2	1311	1298
5	4	921	843
5	6	1610	1686
****K =		8******	
1	3	443	-683
1	5	1740	-2047
1	7	999	982
1	9	531	-536
1	11	782	619
2	0	2444	2444
2	2	553	615
2	4	768	752
2	6	684	-600
2	8	424	483
3	1	507	-353
3	3	886	-727
3	5	1321	-1382
3	7	1050	861
4	0	1998	2061
*4	2	279	192
4	4	639	418

[a] Starred reflections are those which were unobserved but were assigned half the minimum observed value.

for the two oxygen atoms, all in the 16-fold general positions $(0, 0, 0;\ ^1/_2, ^1/_2, ^1/_2) \pm (x, y, z;\ \bar{x}, ^1/_2 - y, z;\ ^3/_4 - y, ^1/_4 + x, ^1/_4 + z;\ ^1/_4 + y, ^1/_4 - x, ^1/_4 + z)$. A third Fourier synthesis phased on these 18 atoms indicated the location of the three fluorine atoms and the carboxyl carbon atom. Subsequent Fourier maps, as well as a difference map, gave no definite indication of the position of the trifluoromethyl carbon atom. However, since its position was approximately fixed by the three fluorine atoms and the carboxyl carbon atom, its positional parameters were calculated for the initial cycles of Fourier refinement by assuming a C–C distance of 1.57 A, directed toward the centroid of the fluorine atoms. A cycle of full-matrix, least-squares refinement, with these 21 atoms, each having an isotropic temperature factor of the form $\exp(-B \sin^2 \theta/\lambda^2)$, resulted in an R value of 0.14 after four cycles of refinement. The next cycle of refinement, in which less weight was given to the low-intensity reflections (as explained earlier), caused a further decrease of R to 0.12. Two more cycles of refinement, with anisotropic temperature factors for the trifluoroacetate ions, were carried out. All parameter variations were now less than one-third of 1 standard deviation. It was therefore apparent that convergence had been reached, the final residual, R, being 0.105. The observed and final calculated structure factors, $|F_o|$ and F_c, are contained in Table I. The final positional parameters, along with the isotropic temperature factors, are given in Table II.

TABLE II

POSITIONAL AND THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x/a (σ)	y/a (σ)	z/c (σ)	B (σ), A²
Co	0.000	0.250	0.1250	6 (1)
As	0.500	0.750	0.2163 (1)	3 (1)
O_1	0.128 (2)	0.258 (2)	0.1573 (4)	5 (1)
O_2	0.265 (2)	0.275 (2)	0.1214 (7)	8 (1)
C_1	0.229 (3)	0.260 (3)	0.1487 (12)	8 (1)
C_2	0.298 (4)	0.255 (7)	0.1838 (18)	11 (2)
F_1	0.256 (3)	0.260 (5)	0.2095 (6)	12 (1)
F_2	0.362 (3)	0.170 (3)	0.1786 (6)	14 (1)
F_3	0.367 (3)	0.349 (3)	0.1798 (7)	15 (1)
C_{11}[a]	0.366 (2)	0.738 (2)	0.1883 (6)	3 (1)
C_{12}	0.358 (2)	0.835 (2)	0.1654 (7)	5 (1)
C_{13}	0.261 (3)	0.828 (3)	0.1435 (8)	7 (1)
C_{14}	0.182 (3)	0.734 (3)	0.1483 (7)	6 (1)
C_{15}	0.194 (3)	0.642 (3)	0.1696 (7)	5 (1)
C_{16}	0.291 (3)	0.652 (3)	0.1923 (7)	6 (1)
C_{21}	0.493 (2)	0.620 (2)	0.2438 (6)	4 (1)
C_{22}	0.424 (3)	0.615 (3)	0.2708 (7)	5 (1)
C_{23}	0.423 (2)	0.519 (3)	0.2936 (6)	4 (1)
C_{24}	0.491 (3)	0.429 (3)	0.2860 (7)	5 (1)
C_{25}	0.568 (3)	0.431 (3)	0.2587 (9)	8 (1)
C_{26}	0.571 (3)	0.535 (3)	0.2361 (8)	7 (1)

[a] C_{ij} corresponds to the jth carbon of the ith phenyl.

Table III

Anisotropic Thermal Parameters[a] (×2000)

Atom	β_{11} (σ)	β_{22} (σ)	β_{33} (σ)	β_{12} (σ)	β_{13} (σ)	β_{23} (σ)
O_1	18 (5)	41 (6)	1 (1)	15 (5)	−1 (1)	1 (1)
O_2	19 (6)	49 (8)	2 (1)	−5 (5)	4 (5)	1 (2)
C_1	2 (7)	12 (6)	6 (1)	6 (6)	8 (3)	1 (2)
C_2	4 (9)	63 (19)	7 (2)	23 (11)	−13 (4)	−3 (6)
F_1	39 (9)	154 (20)	2 (1)	12 (10)	−3 (1)	−3 (4)
F_2	37 (8)	96 (13)	3 (1)	40 (10)	−4 (2)	5 (2)
F_3	51 (9)	63 (12)	4 (1)	−6 (10)	−7 (2)	2 (2)

[a] These are the coefficients in the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV

Interatomic Distances and Angles and Their Estimated Standard Deviations

Interatomic distances	Values, A	Angles	Deg
Co–O_1	2.00 (3)	O_1–Co–O_1*[a]	97 (2)
Co–O_2	3.11 (3)	O_2–Co–O_2*[a]	163 (2)
O_1–C_1	1.23 (4)	O_1–C_1–O_2	127 (3)
O_2–C_1	1.21 (6)	O_1–C_1–C_2	103 (4)
C_1–C_2	1.65 (8)	O_2–C_1–C_2	130 (4)
C_2–F_1	1.16 (8)	C_1–C_2–F_1	125 (4)
C_2–F_2	1.26 (8)	C_1–C_2–F_2	100 (5)
C_2–F_3	1.37 (8)	C_1–C_2–F_3	99 (5)
F_1–F_2	2.06 (5)	F_1–C_2–F_2	117 (5)
F_1–F_3	2.06 (5)	F_1–C_2–F_3	109 (5)
F_2–F_3	2.09 (5)	F_2–C_2–F_3	105 (5)
As–C_{11}[b]	1.95 (2)	F_1–F_2–F_3	60 (1)
As–C_{21}	1.89 (3)	F_1–F_3–F_2	60 (1)
C_{11}–C_{12}	1.47 (4)	C_{11}–As–C_{21}	105 (2)
C_{12}–C_{13}	1.45 (4)	C_{11}–As–C_{11}*[c]	109 (2)
C_{13}–C_{14}	1.44 (5)	C_{21}–As–C_{21}*[c]	107 (2)
C_{14}–C_{15}	1.39 (4)	As–C_{11}–O_{12}	112 (2)
C_{15}–C_{16}	1.47 (4)	As–C_{11}–C_{22}	120 (2)
C_{16}–C_{11}	1.34 (4)	As–C_{21}–C_{22}	123 (2)
C_{21}–C_{22}	1.37 (4)	As–C_{21}–C_{26}	115 (2)
C_{22}–C_{23}	1.45 (4)	C_{11}–C_{12}–C_{13}	113 (3)
C_{23}–C_{24}	1.36 (4)	C_{12}–C_{13}–C_{14}	117 (3)
C_{24}–C_{25}	1.43 (5)	C_{13}–C_{14}–C_{15}	128 (3)
C_{25}–C_{26}	1.52 (5)	C_{14}–C_{15}–C_{16}	114 (3)
C_{26}–C_{21}	1.39 (5)	C_{15}–C_{16}–C_{11}	119 (3)
		C_{16}–C_{11}–C_{12}	128 (3)
		C_{21}–C_{22}–C_{23}	124 (3)
		C_{22}–C_{23}–C_{24}	116 (3)
		C_{23}–C_{24}–C_{25}	122 (3)
		C_{24}–C_{25}–C_{26}	120 (3)
		C_{25}–C_{26}–C_{21}	115 (3)
		C_{26}–C_{21}–C_{22}	122 (3)

[a] O_1 is related to O_1* by a twofold axis. [b] C_{ij} corresponds to the *j*th carbon of the *i*th phenyl. [c] C_{ij}* is related to C_{ij} by a twofold axis.

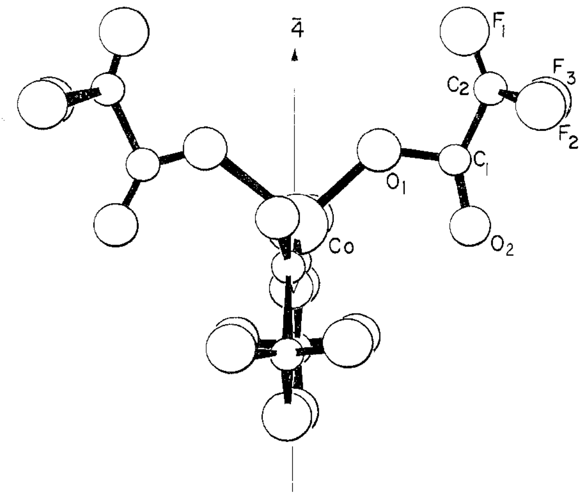

Figure 1.—The (010) projection of the $Co(O_2CCF_3)_4^{2-}$ ion as it occurs in the tetraphenylarsonium salt.

The anisotropic temperature factors are given in Table III.

Coordination of Cobalt(II).—A (010) projection of the $Co(CF_3COO)_4^{2-}$ ion is given in Figure 1. Interatomic distances and angles are given in Table IV. The atoms are numbered as in Figure 1. As in the case of the $Co(NO_3)_4^{2-}$ ion,[2] the eight oxygen atoms may be considered to occupy the corners of a D_{2d} dodecahedron. Four oxygen atoms occupy the A positions (*cf.* Figure 2 of ref 2) at a distance of 2.00 ± 0.03 A while four others occupy the B positions at 3.11 ± 0.03 A. In contrast to the $Co(NO_3)_4^{2-}$ case, however, the dodecahedron has been distorted almost to the limit, in the sense that the four oxygen atoms at the A positions are approximately at the corners of a tetrahedron, the O_1–Co–O_1 angles being 97°, while the four at the B positions are very far away.

The Trifluoroacetate Ion.—The structure of this ligand is relative poorly defined in this study, especially in regard to the position of the carbon atom (C_2) of the CF_3 group and the dimensions of the CF_3 group in general. This inexactness stems from the large amplitude of the anisotropic thermal motions of the fluorine atoms, which can be seen very strikingly in Figure 2. Dimensions not involving C_2 are in satisfactory agreement with those reported[7] for CF_3COONH_4. The nonpositive definite form of the thermal tensors for C_1 and C_2 can perhaps be traced in part to the existence of pseudo-mirror planes parallel to (100) and (001), these mirrors being destroyed chiefly by the rotation of the phenyl groups, as shown in Figure 3, although the generally large amount of thermal motion in the CF_3 group probably contributes also.

The Tetraphenylarsonium Ions.—The phenyl groups are hexagonal and planar within experimental error. The mean planes in each case pass through C_{i1} and C_{i4} and the mean deviations of the other four carbon atoms from each one are about ±0.03 A. The mean C–C distance is 1.42 ± 0.01 A. The average of the As–C distances, 1.92 ± 0.03 A, is in good agreement with the sum of covalent radii, 1.93 A. The rotational orientations of the planes of the

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(7) D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J. Chem. Soc.*, 1303 (1964).

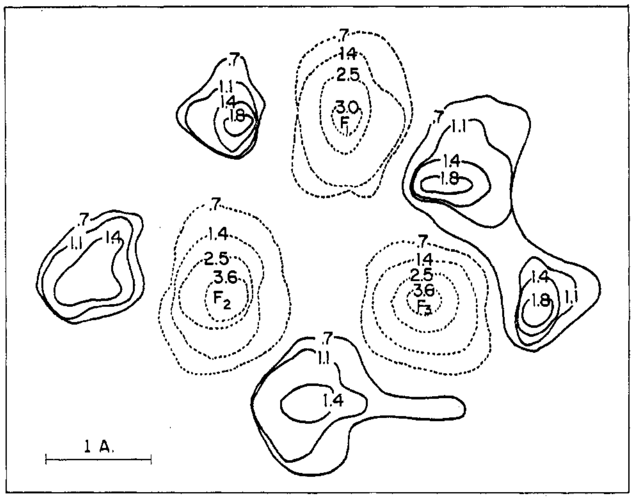

Figure 2.—A section through the three-dimensional electron density difference map, passing through the centers of the three fluorine atoms, after refinement with isotropic temperature factors. The dotted lines represent negative regions. Contours are given in units of electrons per cubic angstrom.

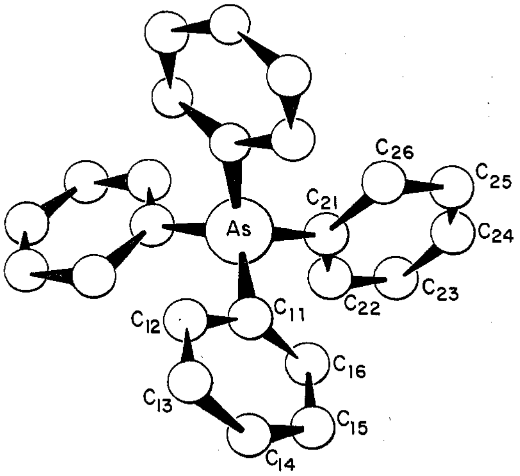

Figure 3.—A projection of the $(C_6H_5)_4As^+$ ion down the two-fold axis. The pseudo-mirror planes referred to in the text contain the As, C_{i1}, and C_{i4} atoms.

phenyl groups are 45 and 32° from the vertical (*i.e.*, from planes parallel to the *c* axis of the crystal). The tetraphenylarsonium ions have approximately S_4 symmetry; they would have this symmetry rigorously were the two different tilt angles of the rings equal. This result is in accord with the structural data for the $(C_6H_5)_4As^+$ ion in other compounds, which have recently been discussed in detail.[8]

Spectroscopic and Magnetic Data.—The visible and near-infrared absorption spectra are shown in Figure 4. These spectra are very similar to those of $Co(NO_3)_4^{2-}$, though somewhat more intense and somewhat more structured. They closely resemble the spectra of several other tetrahedral Co(II) complexes in which the ligands are bound through oxygen, such as the $Co[(C_6H_5)_3PO]_4^{2+}$ ion[9] and the $Co\{[(CH_3)_2N]_3PO\}_4^{2+}$ ion,[10] although there are some qualitative differences, mainly in the ratio of the intensities, $f(\nu_3)/f(\nu_2)$, from the spectra of cobalt dipivaloylmethanide and monomeric bis(acetylacetonato)cobalt.[11] The usual electronic structure parameters[9] are collected in Table V.

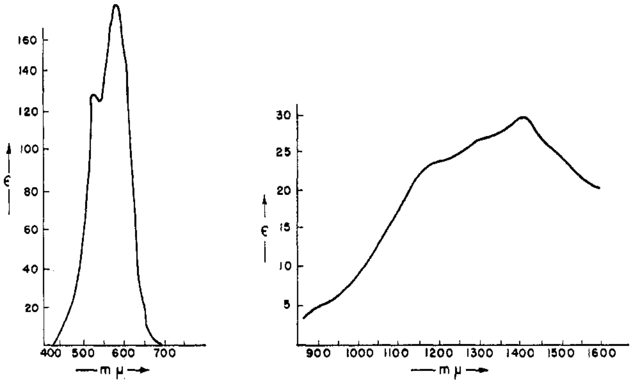

Figure 4.—The electronic absorption bands of the $Co(O_2CCF_3)_4^{2-}$ ion, recorded on a 0.01 *M* solution in acetonitrile.

TABLE V

ELECTRONIC STRUCTURE PARAMETERS

ν_2	7100 cm^{-1}
ν_3	17,400 cm^{-1}
Δ	4090 cm^{-1}
B'	815 cm^{-1}
β[a]	0.84
$f(\nu_2)$	4.3×10^{-4}
$f(\nu_3)$	2.62×10^{-3}
μ[b]	4.55 BM
λ'	174 cm^{-1}

[a] $\beta = B'/B$; $B = 967$ cm^{-1}. [b] From Curie–Weiss law with $\theta = 10°$.

Discussion

The structure of the $Co(O_2CCF_3)_4^{2-}$ ion bears an interesting relationship to that of $Co(NO_3)_4^{2-}$ and to that of $Ti(NO_3)_4$.[12] The structure of $Ti(NO_3)_4$ is such that the eight coordinated oxygen atoms lie at the vertices of a D_{2d} dodecahedron in which the A and B Ti–O bonds[13] are essentially equal. In $Co(NO_3)_4^{2-}$, the A bonds are of approximately normal length (~2.07 A) while the mean length (2.45 A) of the B bonds is considerably greater. In $Co(O_2CCF_3)_4^{2-}$ this trend toward lengthening of the B bonds goes much further, so that the oxygen atoms in the B positions can be considered only very loosely bonded. It is difficult, if not impossible, to be definite as to the distance beyond which they should be considered as not bonded at all, but we believe that the distance of 3.11 A must be close to it. At the same time the vertical angle of 97° is not farther from the ideal tetrahedral angle than that in other truly four-coordinate complexes which would be unreservedly regarded as "tetrahedral."

The electronic structure parameters, Δ_t, μ, λ', and the

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(8) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).

(9) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

(10) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(11) F. A. Cotton and R. H. Soderberg, *ibid.*, **3**, 1 (1964).

(12) C. C. Addison, D. C. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 367 (1964); S. C. Wallwork and C. C. Addison, private communication.

(13) See ref 2 for a drawing of the dodecahedron in which the A and B positions are indicated.