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The Crystal Structure of Dicobalt Octacarbonyl*

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The crystal structure of dicobalt octacarbonyl has been determined and refined by two cycles of three-dimensional, isotropic, least-squares calculations. The crystals are monoclinic, space group $P2_1/m$ with $a=6\cdot62$, $b=15\cdot59$, $c=11\cdot31$ Å and $\beta=90°0'\pm20'$. There are two pairs of crystallographically independent molecules per unit cell. The measured density was 1·87 g.cm^{-3}.

The molecular structure of $Co_2(CO)_8$ is very nearly that of $Fe_2(CO)_9$ less one bridge carbonyl group. The consequent lack of trigonal molecular symmetry results in a crystal structure which is a slightly rearranged $Fe_2(CO)_9$ structure.

Introduction

At the time this work was begun, at least six configurations for the dicobalt octacarbonyl molecule had been proposed. The first structure (Syrkin & Dyatkina, 1950) had D_{2h} symmetry and was based purely on theoretical considerations. On the basis of infrared and ultraviolet data (Cable, Nyholm & Sheline, 1954; Friedel, Wender, Shufler & Sternberg, 1955) five additional structures with D_{2h}, C_{2h}, and C_{2v}, D_{3h}, D_{3d} symmetries, respectively, were proposed. Meanwhile Cavalca & Bassi (1953) had reported the results of an incomplete X-ray diffraction study based on a single Patterson projection. In addition to providing cell dimensions, they concluded that the space group was $P2_1$ or $P2_1/m$, and that the molecule was bridged and had the symmetry $2/m$ or mm.

The only binuclear metal carbonyl whose structure had been completely determined at this date was iron enneacarbonyl (Powell & Ewens, 1939). Clearly, dicobalt octacarbonyl needed a thorough investigation to determine its structure, the bridging arrangement, if present, and the extent of the similarity between the $Co_2(CO)_8$ and $Fe_2(CO)_9$ structures. We report here the complete analysis of the structure of $Co_2(CO)_8$ which proves to have the molecular symmetry $C_s=m$, different from any of the six structures previously proposed. A very considerable similarity between the $Co_2(CO)_8$ and the $Fe_2(CO)_9$ structures is demonstrated.

Preliminary investigation

Dicobalt octacarbonyl crystals are orange platelets or laths, best obtained by vacuum sublimation. The crystals must be immediately sealed in capillary tubes or otherwise protected from the air to prevent decomposition. They are biaxial positive. An extinction angle of 23° to [100], which is the direction of elongation, is observed for the (010) platey habit. The unit-cell dimensions found were

$$a=6\cdot62\pm0\cdot03,\ b=15\cdot59\pm0\cdot03\ ,$$
$$c=11\cdot31\pm0\cdot03\ \text{Å};\ \beta=90°\ 0'\pm20'\ ,$$

corresponding to 4 molecules per unit cell. The measured density was 1·87 g.cm^{-3}, while the X-ray density was 1·95 g.cm^{-3}. The systematic absence was $0k0$, k odd; in addition, most of the $hk0$ reflections with h odd were absent. Of the two possible space groups $P2_1$ and $P2_1/m$, the correct one was found to be $P2_1/m$ with a strong pseudo a-glide parallel to (001).

Structure determination

Two-dimensional methods of analysis were largely unsuccessful when applied to this structure. However, it was found that there were two sets of crystallographically independent molecules in the unit cell and that the intramolecular cobalt–cobalt vectors were about 2·54 Å long and parallel to [010], all in agreement with the work of Cavalca & Bassi. Packing considerations showed that some variant of the trigonally arranged bridges of the iron enneacarbonyl structure was more favorable than the bridging arrangements

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* This paper is based on the Ph.D. thesis of G. Gardner Sumner.

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Table 1. *Observed and calculated structure factors based on final least-squares parameters*

h	k	ℓ	10 F_o	10 F_c
0	0	1	306	-321
0	0	2	1141	1412
0	0	3	616	-682
0	0	4	431	-415
0	0	5	401	-452
0	0	6	1255	-1408
0	0	7	168	-62
0	0	8	844	-899
0	0	9	393	415
0	0	10	123	-149
0	0	11	461	525
0	1	1	400	446
0	1	2	1191	1553
0	1	3	123	125
0	1	4	1404	1706
0	1	5	293	-320
0	1	6	577	551
0	1	7	618	-592
0	1	8	316	-330
0	1	9	328	-325
0	1	10	402	-433
0	1	13	188	213
0	2	0	1055	-1133
0	2	1	71	84
0	2	2	710	-800
0	2	3	206	170
0	2	4	208	201
0	2	5	330	324
0	2	6	401	415
0	2	8	385	378
0	2	9	210	-224
0	2	11	240	-218
0	3	1	215	-282
0	3	2	170	-221
0	3	3	109	106
0	3	4	100	98
0	3	6	135	141
0	3	7	122	-165
0	4	0	1328	-1601
0	4	1	238	-261
0	4	2	499	-474
0	4	2	497	-474
0	4	3	509	549
0	4	5	183	204
0	4	6	370	355
0	4	8	381	353
0	4	9	195	-219
0	4	10	58	61
0	5	1	664	681
0	5	2	925	-920
0	5	3	106	-92
0	5	4	616	-448
0	5	5	320	330
0	5	6	235	-217
0	5	7	474	451
0	5	8	223	154
0	5	9	272	290
0	5	10	101	97
0	5	13	209	-221
0	6	0	152	-245
0	6	1	175	168
0	6	2	746	813
0	6	3	333	-230
0	6	4	149	-121
0	6	5	540	-533
0	6	6	407	-375
0	6	8	352	-270
0	6	9	279	308
0	6	11	288	269
0	7	1	136	155
0	7	2	704	675
0	7	4	721	643
0	7	5	302	-299
0	7	6	268	225
0	7	7	508	-520
0	7	9	211	-213
0	8	0	219	-160
0	8	1	92	93
0	8	2	356	-329
0	8	3	61	66
0	8	4	104	100
0	8	5	212	181
0	8	6	378	297
0	8	9	129	-125
0	9	2	85	-55
0	9	3	73	-60
0	9	4	182	-178
0	9	6	71	-55
0	10	0	558	-458
0	10	1	98	92
0	10	2	176	-212
0	10	4	113	95
0	10	5	182	164
0	10	6	214	221
0	11	1	285	-290
0	11	2	465	-465
0	11	4	665	-608
0	11	5	203	165
0	11	6	216	-195
0	11	7	286	284
0	12	0	988	871
0	12	2	525	445
0	12	3	229	-212
0	12	4	154	-130
0	12	5	205	-172
0	12	6	455	-400
0	12	8	262	-256
0	12	9	239	203
0	12	11	255	228
0	13	2	559	484
0	13	4	552	508
0	13	6	182	155
0	13	9	217	-184
0	14	0	623	-520
0	14	2	289	-220
0	14	3	181	194
0	14	4	62	51
0	14	6	234	205
0	14	8	238	197
1	0	0	122	114
1	0	1	881	-1001
-1	0	1	799	751
1	0	2	274	-283
-1	0	2	291	247
1	0	3	264	-130
-1	0	3	717	620
1	0	4	143	74
-1	0	4	146	-187
1	0	5	685	-589
-1	0	5	774	690
1	0	6	431	371
-1	0	6	602	-558
1	0	7	219	-177
-1	0	7	184	-124
1	0	8	524	525
-1	0	8	650	-571
1	0	9	376	332
-1	0	9	443	-368
1	0	10	207	218
1	0	12	208	-217
-1	0	12	137	183
1	1	1	1315	1583
-1	1	1	1290	-1726
1	1	2	146	-122
-1	1	2	439	473
1	1	3	445	434
-1	1	3	140	118
1	1	4	509	-509
-1	1	4	621	574
1	1	5	450	-390
-1	1	5	554	434
1	1	6	323	-340
-1	1	6	172	140
1	1	7	591	-540
-1	1	7	618	570
1	1	8	292	244
-1	1	8	110	-140
1	1	9	323	-275
-1	1	9	305	280
1	1	10	348	377
-1	1	10	429	-455
-1	1	12	258	-260
1	2	1	552	655
-1	2	1	252	-183
1	2	2	458	533
-1	2	2	149	157
1	2	3	1012	1047
-1	2	3	662	-595
1	2	4	391	-398
-1	2	4	312	-277
1	2	5	497	425
-1	2	5	420	-430
1	2	6	260	-264
-1	2	6	360	365
1	2	7	234	-269
-1	2	7	308	-351
1	2	8	228	-226
-1	2	8	314	327
1	2	9	174	-172
-1	2	9	190	158
1	3	1	55	65
-1	3	1	161	138
1	3	2	178	-118
-1	3	2	394	-412
1	3	3	1214	1380
-1	3	3	1461	1719
1	3	4	90	-91
1	3	5	103	133
1	3	7	155	111
-1	3	7	128	-84
1	4	1	261	250
-1	4	1	629	-683
1	4	2	152	-184
1	4	3	156	139
-1	4	3	654	-632
-1	4	4	74	80
1	4	5	469	526
-1	4	5	199	-131
1	4	6	164	-126
-1	4	6	275	236
1	4	7	267	256
-1	4	7	266	266
1	4	8	279	-264
-1	4	8	312	238
1	4	9	204	-192
-1	4	9	134	158
1	5	1	1410	-1569
-1	5	1	1272	1427
1	5	2	124	-170
-1	5	2	92	-69
1	5	3	490	-508
-1	5	3	145	120
1	5	4	491	448
-1	5	4	571	-539
1	5	5	329	329
-1	5	5	669	-730
1	5	6	272	290
-1	5	6	223	-185
1	5	7	654	677
-1	5	7	659	-642
1	5	8	154	-147
-1	5	8	187	197
1	5	9	196	230
-1	5	9	253	-230
1	5	10	268	-294
-1	5	10	256	277
1	5	12	221	-220
-1	5	12	226	205
1	6	1	665	-656
-1	6	1	645	652
1	6	3	1533	-1720
-1	6	3	1486	1563
1	6	4	105	103
-1	6	4	91	-88
1	6	5	915	-902
-1	6	5	770	732
1	6	6	574	617
-1	6	6	546	-533
-1	6	7	113	87
1	6	8	421	434
-1	6	8	443	-451
1	6	9	258	282
-1	6	9	190	-207
-1	6	10	149	-155
1	6	11	229	234
-1	6	11	190	-191
1	6	12	156	-152
-1	6	12	169	174
1	6	14	193	-220
1	7	1	1008	982
-1	7	1	996	-953
1	7	2	210	-201
1	7	3	304	248
-1	7	3	400	-413
1	7	4	278	-285
-1	7	4	303	286
1	7	5	700	-675
-1	7	5	412	411
-1	7	6	471	467
1	7	7	563	-547
-1	7	7	513	471
-1	7	8	200	-204
1	7	9	167	-166
-1	7	9	146	142
1	7	10	291	301
-1	7	10	285	-272
1	7	12	187	189
-1	7	12	211	-222
1	8	1	225	165
-1	8	1	268	-251
1	8	2	154	-141
-1	8	2	315	-323
1	8	3	662	648
-1	8	3	761	-705
1	8	4	218	213
-1	8	4	319	295
1	8	5	347	310
-1	8	5	574	-481
1	8	6	291	-316
-1	8	6	188	194
1	8	7	124	115
1	8	8	213	-240
-1	8	8	171	187
1	9	2	169	181
-1	9	2	128	101
1	9	3	380	-302
-1	9	3	322	-272
1	10	1	235	202
1	10	3	200	299
-1	10	3	241	-207
-1	10	5	271	-243
1	10	6	279	-247
-1	10	6	189	146
1	11	1	479	-424
-1	11	1	518	449
1	11	2	117	107
-1	11	2	176	-137
-1	11	3	305	285
1	11	4	158	141
-1	11	4	221	-160
1	11	5	396	343
-1	11	5	156	-110
-1	11	6	247	-235
1	11	7	260	244
-1	11	7	236	-223
1	11	10	215	-192
-1	11	10	250	210
1	12	1	308	-289
-1	12	1	255	214
1	12	2	159	-162
-1	12	2	129	140
1	12	3	599	-548
-1	12	3	525	464
1	12	5	336	-291
-1	12	5	447	392
1	12	6	203	190
-1	12	6	247	-219
1	12	8	246	238
-1	12	8	286	-265
1	13	1	551	482
-1	13	1	590	-532
-1	13	2	207	173
-1	13	3	281	-232
1	13	4	178	-177
-1	13	4	280	252
1	13	5	222	-223
-1	13	5	264	212
1	13	6	154	-154
1	13	7	310	-268
-1	13	7	308	268
1	13	10	234	225
-1	13	10	239	-231
1	14	1	219	201
-1	14	1	178	-160
1	14	3	342	305
-1	14	3	296	-262
1	14	5	257	212
-1	14	5	193	-189
-1	14	8	186	163
2	0	0	838	-796
2	0	1	482	-570
-2	0	1	156	194
2	0	2	1064	-1277
-2	0	2	939	-1062
2	0	3	510	534
-2	0	3	577	556
2	0	4	288	230
-2	0	4	106	84
2	0	5	443	428
-2	0	5	518	496
2	0	6	614	675
-2	0	6	461	454
2	0	7	129	-102
-2	0	7	184	144
2	0	8	572	521
-2	0	8	555	485
2	0	9	316	-380
-2	0	9	388	-393
-2	0	10	74	97
2	0	11	298	-294
-2	0	11	311	-321
-2	0	12	104	-66
-2	0	13	177	-159
2	1	0	493	-538
2	1	1	121	86
-2	1	1	237	253
2	1	2	990	-1077
-2	1	2	1086	-1168
2	1	3	73	58
-2	1	3	286	-243
2	1	4	804	-745
-2	1	4	713	-589
2	1	5	259	277
-2	1	5	315	280
2	1	6	273	-266
-2	1	6	292	-296
2	1	7	408	403
-2	1	7	500	464
2	1	8	252	250
-2	1	8	160	109
2	1	9	258	257
-2	1	9	318	315
2	1	10	128	176
2	1	13	189	-216
-2	1	13	172	-186
2	2	0	822	905
2	2	1	231	216
-2	2	1	384	-364
2	2	2	532	501
-2	2	2	403	361
2	2	3	188	-171
-2	2	3	289	-306
2	2	4	77	70
-2	2	4	300	-286
-2	2	5	255	-232
2	2	6	391	-352
-2	2	6	476	-438
-2	2	7	113	-66
2	2	8	255	-240
-2	2	8	185	-123
2	2	9	144	158
-2	2	9	201	177
2	2	11	150	194
-2	2	11	181	187
2	3	0	1345	-1660
2	3	1	175	150
2	3	3	174	307
-2	3	3	99	-136
2	3	4	89	119
-2	3	4	87	93
-2	3	5	150	175
2	3	6	207	214
2	3	8	194	191
-2	3	8	165	-172
2	4	0	718	627
2	4	1	61	54
-2	4	1	157	-147
2	4	2	263	266
-2	4	2	211	188
-2	4	4	129	-138
2	4	5	265	-276
-2	4	5	200	-220
2	4	6	246	-259
-2	4	6	222	-179
-2	4	8	242	-230
-2	4	11	168	158
2	5	0	221	243
2	5	1	330	376
-2	5	1	372	431
2	5	2	516	468
-2	5	2	562	509
-2	5	3	89	30
2	5	4	790	812
-2	5	4	779	757
2	5	5	239	-248
-2	5	5	333	-287
2	5	6	421	323
-2	5	6	204	210
2	5	7	469	-456
-2	5	7	588	-508
2	5	8	222	-201
2	5	9	152	-165
-2	5	9	210	-211
2	5	10	199	-222
-2	5	10	219	-212
2	6	0	1506	-1640
2	6	1	168	183
-2	6	1	164	90
2	6	2	657	-566
-2	6	2	628	-590
2	6	3	122	71
-2	6	3	318	299
2	6	4	102	75
-2	6	4	406	331
2	6	5	314	301
-2	6	5	491	444
2	6	6	653	611
-2	6	6	738	640
2	6	8	348	348
-2	6	8	362	354
2	6	9	256	-245
-2	6	9	292	-286
2	6	10	153	104
2	6	11	305	-332
-2	6	11	384	-350
2	7	0	151	172
-2	7	1	258	-253
2	7	2	851	-903
-2	7	2	773	-692
2	7	3	179	-248
-2	7	3	81	75
2	7	4	946	-944
-2	7	4	1002	-1006
2	7	5	309	260
-2	7	5	221	218
2	7	6	312	-244
-2	7	6	350	-318
2	7	7	361	368
-2	7	7	415	421
-2	7	8	201	179
2	7	9	248	271
-2	7	9	267	240
2	7	10	266	251
-2	7	10	254	213
2	8	0	702	700
2	8	1	257	-234
-2	8	1	219	236
2	8	2	411	362
-2	8	2	610	615
2	8	3	158	-183
-2	8	3	276	-285
2	8	4	333	-346
2	8	5	163	-199
-2	8	5	270	-253
2	8	6	418	-418
-2	8	6	327	-282
2	8	8	311	-294
-2	8	8	264	-275
2	8	9	199	200
-2	8	9	168	200
-2	8	11	186	199
2	9	0	375	343

based on dsp^3 hybridization, in which the bridge carbonyl atoms were all coplanar.

Weissenberg data were obtained with cobalt radiation for the spectra *hkl*, from $h=0$ through 4. The spot intensities were measured photometrically and modified by empirically determined Weissenberg distortion corrections for upper levels. Several possible combinations of cobalt positions were obtained from the

Table 1. (*cont.*)

h	k	ℓ	10 F_o	10 F_c
-2	9	1	158	150
2	9	2	252	221
2	9	4	230	216
-2	9	4	269	254
-2	9	6	157	135
2	10	0	230	237
2	10	2	295	254
-2	10	2	232	252
2	10	3	135	-115
-2	10	3	230	-217
-2	10	5	208	-143
2	10	6	166	-162
-2	10	6	144	-144
2	10	8	174	-179
-2	10	8	98	-100
-2	10	9	180	135
2	11	0	142	-118
2	11	2	621	613
-2	11	2	529	454
2	11	4	486	452
-2	11	4	507	475
2	11	5	211	-157
-2	11	6	226	197
2	11	7	204	-190
-2	11	7	234	-221
-2	11	8	157	-141
2	11	9	184	-181
-2	11	9	173	-153
2	12	0	675	-639
2	12	2	440	-396
-2	12	2	554	-501
2	12	3	212	188
-2	12	3	290	257
2	12	4	207	224
-2	12	5	249	228
2	12	6	404	391
-2	12	6	348	322
2	12	8	301	277
-2	12	8	217	213
2	12	9	193	-200
-2	12	9	208	-194
-2	12	11	199	-203
2	13	2	458	-398
-2	13	2	399	-376
2	13	4	482	-427
-2	13	4	440	-390
-2	13	5	179	154
-2	13	6	191	-155
2	13	7	210	217
-2	13	7	272	245
-2	13	9	188	169
2	14	0	298	266
2	14	2	212	195
-2	14	2	154	141
2	14	6	157	-139
-2	14	6	184	-155
2	16	0	219	171
3	0	0	100	-41
3	0	1	609	579
-3	0	1	365	-272
-3	0	2	100	108
3	0	3	1397	1572
-3	0	3	1441	-1586
3	0	4	227	-211
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3	0	6	458	-452
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3	0	7	83	-50
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3	0	8	343	-387
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3	0	9	224	-248
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3	2	8	221	234
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3	3	5	305	-306
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3	5	4	103	-82
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3	5	5	447	-490
-3	5	5	379	302
-3	5	6	311	291
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3	5	8	156	136
-3	5	9	184	198
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-3	5	10	328	-297
-3	5	12	203	-201
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-3	12	5	338	-297
3	12	6	211	-180
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3	13	7	229	235
-3	13	7	210	-201
3	14	1	187	-157
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-3	14	3	286	253
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-4	0	3	234	-207
4	0	4	228	-222
-4	0	4	197	-183
4	0	5	210	-210
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4	0	6	571	-617
-4	0	6	528	-435
-4	0	7	108	-61
4	0	8	190	-231
-4	0	8	168	-188
4	0	9	183	203
-4	0	9	225	209
4	0	10	128	-86
4	0	11	228	256
-4	0	11	310	305
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4	1	5	298	-270
-4	1	5	230	-194
4	1	6	332	265
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4	1	7	350	-365
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-4	1	9	187	-207
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4	2	6	277	271
-4	2	6	281	244
4	2	8	209	239
-4	2	9	156	-169
-4	2	11	159	-151
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4	3	2	176	225
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4	4	6	299	316
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-4	4	9	147	-114
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4	5	5	166	113
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-4	5	6	286	-282
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4	6	8	373	-361
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4	6	9	247	242
-4	6	9	275	277
-4	6	11	227	253
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4	7	6	131	144
-4	7	6	200	201
4	7	7	163	-177
-4	7	7	254	-255
-4	7	9	256	-227
4	8	0	452	-469
-4	8	2	284	-258
4	8	3	117	134
4	8	4	102	108
4	8	6	142	165
4	8	8	159	123
-4	8	8	159	134
4	10	0	283	-283
4	10	2	141	-122
4	11	2	196	-193
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4	11	4	237	-262
-4	11	4	202	-224
-4	11	7	226	183
4	12	0	392	390
4	12	2	229	228
-4	12	2	202	207
4	12	4	96	-110
-4	12	5	205	-204
4	12	6	201	-228
-4	12	6	179	-176
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4	13	4	360	327
-4	13	4	355	316
-4	13	5	147	-116
-4	13	7	225	-210
4	14	0	237	-218
4	14	2	220	-192
-4	14	2	167	-161
-4	14	5	160	148
-4	14	6	162	126
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-5	0	1	337	356
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5	0	4	81	-46
5	0	5	637	-670
-5	0	5	595	596
5	0	6	326	343
-5	0	6	360	-383
5	0	8	175	229
-5	0	8	249	-274
-5	0	9	172	-169
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-5	1	2	212	191
5	1	3	130	117
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5	1	5	370	-426
-5	1	5	378	372
-5	1	6	237	228
5	1	7	290	-329
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5	2	1	217	233
5	2	3	406	406
-5	2	3	371	-368
5	2	5	227	249
-5	2	5	210	-208
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-5	2	8	166	150
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5	5	1	321	-367
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5	5	4	176	194
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-5	5	5	135	-146
5	5	7	228	270
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5	6	1	223	-270
-5	6	1	154	163
5	6	3	391	-487
-5	6	3	346	381
5	6	5	185	-211
-5	6	5	184	201
-5	6	6	160	-168
-5	6	8	315	-290
5	7	1	376	397
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-5	7	4	214	229
5	7	5	170	-205
5	7	7	257	-283
-5	7	7	234	229
5	8	1	224	233
5	8	3	179	206
-5	8	3	131	-143
-5	8	5	181	-173
-5	8	6	140	128
5	10	1	198	168
-5	10	5	124	-137
5	11	1	309	-285
-5	11	1	397	364
5	11	7	154	176
5	12	1	264	-242
5	12	3	374	-348
-5	12	3	335	302
5	12	5	221	-223
-5	12	5	262	236
5	13	1	276	270
-5	13	1	317	-285
6	0	0	298	-370
6	0	2	189	-219
-6	0	2	231	-246
-6	0	3	226	255
-6	0	5	212	201
6	0	6	198	258
-6	0	6	106	156
6	0	8	133	160
6	0	9	155	-142
-6	0	9	162	-171
-6	0	11	146	-171
6	1	2	273	-322
-6	1	2	166	-204
6	1	4	278	-334
-6	1	4	279	-309
-6	1	6	116	-121
-6	1	7	171	209
6	2	0	190	236
-6	2	2	256	258
6	3	0	161	110
6	3	2	135	131
6	4	0	152	202
6	4	2	163	166
-6	4	3	128	-138
6	5	2	309	321
-6	5	2	258	256
6	5	4	301	348
-6	5	4	294	308
6	6	0	482	-504
6	6	2	275	-289
-6	6	2	329	-320
-6	6	3	184	188
6	6	6	290	303
-6	6	6	234	234
6	6	8	179	208
6	7	0	80	-105
6	7	2	338	-355
-6	7	2	332	-342
6	7	4	345	-360
-6	7	4	331	-310
-6	7	7	219	212
6	8	0	324	300
6	8	2	204	211
6	11	2	187	210
6	11	4	184	203
6	12	0	238	-268
7	0	1	218	234
7	0	3	314	374
-7	0	3	218	-249
-7	0	5	187	-189
7	1	1	223	-256
-7	1	1	264	287
-7	1	4	164	-185
7	4	3	151	-147
7	5	1	205	252
-7	5	1	236	-249
7	5	5	168	-198
7	6	3	263	291
-7	6	3	246	-263
7	7	1	185	-237
-7	7	1	223	247
8	0	0	308	313
8	0	8	129	-141

Table 2. *Final atomic parameters with estimated standard deviations, σ (below)*

	Least squares refinement				Differential synthesis refinement			Mean standard deviation* σ
	x/a	y/b	z/c	B	x/a	y/b	z/c	
Co I	0·2426	0·1691	0·4459	3·35 Å^2	0·2429	0·1692	0·4459	
	0·0003	0·0001	0·0002	0·05	0·0002	0·0001	0·0001	0·0012 Å
Co II	0·7522	0·1691	0·9134	3·36	0·7524	0·1691	0·9136	
	0·0003	0·0001	0·0002	0·05	0·0002	0·0001	0·0001	0·0012
*T*O1 I	0·0993	0·1020	0·2166	7·67	0·1115	0·1041	0·2118†	
	0·0019	0·0009	0·0011	0·31	0·0024	0·0011	0·0012	0·0162
*T*O1 II	0·6046	0·1067	0·1452	9·77	0·6110	0·1098	0·1510†	
	0·0020	0·0008	0·0011	0·29	0·0025	0·0012	0·0012	0·0167
*T*O2 I	0·6456	0·0802	0·4377	6·49	0·6449	0·0809	0·4366	
	0·0020	0·0008	0·0011	0·29	0·0016	0·0010	0·0011	0·0130
*T*O2 II	0·1447	0·0769	0·9270	7·39	0·1435	0·0779	0·9281	
	0·0022	0·0009	0·0012	0·30	0·0015	0·0007	0·0012	0·0129
*T*O3 I	0·0346	0·0641	0·6235	6·04	0·0351	0·0637	0·6232	
	0·0020	0·0008	0·0012	0·27	0·0017	0·0005	0·0008	0·0098
*T*O3 II	0·5396	0·0632	0·7336	7·10	0·5448	0·0627	0·7347	
	0·0020	0·0009	0·0011	0·28	0·0028	0·0007	0·0010	0·0141
*B*O1 I	0·4549	0·2500	0·6437	5·77	0·4588	0·2500	0·6420	
	0·0029		0·0016	0·40	0·0015		0·0006	0·0103
*B*O1 II	0·9671	0·2500	0·7168	5·29	0·9661	0·2500	0·7169	
	0·0029		0·0017	0·41	0·0015		0·0005	0·0085
*B*O2 I	0·8463	0·2500	0·4185	6·17	0·8419	0·2500	0·4226†	
	0·0031		0·0015	0·43	0·0017		0·0022	0·0182
*B*O2 II	0·3495	0·2500	0·9272	7·02	0·3487	0·2500	0·9288	
	0·0031		0·0015	0·42	0·0013		0·0012	0·0110
*T*C1 I	0·1542	0·1294	0·3039	5·88	0·1577	0·1306	0·3060	
	0·0023	0·0011	0·0013	0·30	0·0019	0·0009	0·0012	0·0141
*T*C1 II	0·6643	0·1347	0·0563	6·30	0·6616	0·1304	0·0527	
	0·0023	0·0010	0·0013	0·30	0·0028	0·0016	0·0009	0·0181
*T*C2 I	0·4881	0·1184	0·4383	4·41	0·4866	0·1184	0·4381	
	0·0025	0·0010	0·0012	0·30	0·0022	0·0007	0·0009	0·0130
*T*C2 II	0·9950	0·1169	0·9237	4·38	0·9960	0·1164	0·9243	
	0·0025	0·0010	0·0012	0·31	0·0019	0·0007	0·0010	0·0117
*T*C3 I	0·1116	0·1065	0·5516	4·53	0·1128	0·1057	0·5523	
	0·0023	0·0010	0·0013	0·30	0·0019	0·0007	0·0010	0·0130
*T*C3 II	0·6274	0·1041	0·8042	4·45	0·6263	0·1053	0·8057	
	0·0022	0·0011	0·0014	0·30	0·0021	0·0008	0·0011	0·0139
*B*C1 I	0·3518	0·2500	0·5518	4·11	0·3559	0·2500	0·5532	
	0·0034		0·0019	0·43	0·0022		0·0011	0·0139
*B*C1 II	0·8702	0·2500	0·8046	3·51	0·8712	0·2500	0·8052	
	0·0037		0·0019	0·43	0·0015		0·0007	0·0107
*B*C2 I	0·0247	0·2500	0·4298	5·18	0·0275	0·2500	0·4312	
	0·0036		0·0018	0·45	0·0013		0·0012	0·0115
*B*C2 II	0·5287	0·2500	0·9244	5·06	0·5314	0·2500	0·9219	
	0·0034		0·0018	0·44	0·0012		0·0015	0·0128

* Based on differential synthesis refinement.

† Results of second cycle of differential synthesis.

Patterson syntheses $P(U0W)$ and $P(U1/2W)$. The determination of the cobalt x and y coordinates was straightforward with $x_{\rm I} \simeq x_{\rm II} + \frac{1}{2}$ and $y_{\rm I} = y_{\rm II}$, where the subscripts denote crystallographically independent cobalt atoms. The central problem of the structural analysis proved to be the determination of the cobalt $z_{\rm I}$ and $z_{\rm II}$ coordinates whose difference was very roughly $\frac{1}{2}$. This relationship produced overlap in the Patterson sections, and the z coordinates were solved to a first approximation by consideration of the extent of elongation of the superposed vector peaks, and were subsequently improved by trial and error. Iterative Fourier syntheses (Shiono, 1957) followed by two cycles of differential synthesis (Shiono, 1959) resulted in an R value of 0·27 for 1204 reflections including those not observed. The temperature factors used up

Table 3. *Observed and calculated atomic peak heights* (ϱ *in* e.Å^{-3}) *and curvatures* (A_{ij} *in* e.Å^{-5}) *obtained by differential synthesis refinement*

	ϱ	A_{hh}	A_{kk}	A_{ll}	A_{hk}	A_{kl}	A_{lh}
Co I	48·4	−380·8	−395·6	−409·6	2·6	−4·0	17·4
	48·4	−391·7	−376·2	−408·8	2·1	−1·1	13·0
Co II	47·0	−364·5	−385·6	−396·1	−1·6	10·1	27·0
	47·4	−379·2	−371·1	−395·6	−1·1	5·9	17·5
*T*O1 I	5·3	−28·4	−26·9	−33·3	−0·7	−10·5	−5·7
	6·1	−34·1	−33·5	−33·6	−0·6	−7·3	−3·3
*T*O1 II	5·1	−27·8	−25·5	−33·7	6·1	6·3	11·1
	5·4	−28·4	−26·9	−30·0	6·3	1·5	6·7
*T*O2 I	6·8	−44·5	−48·1	−38·2	6·0	−2·5	−2·1
	7·2	−41·5	−46·9	−43·9	4·3	−0·9	−2·1
*T*O2 II	6·5	−46·0	−39·8	−35·8	1·3	3·6	3·2
	6·7	−42·4	−38·2	−38·2	0·2	2·4	3·0
*T*O3 I	7·6	−41·6	−53·2	−53·0	−1·8	6·5	3·2
	7·8	−44·5	−49·4	−53·6	0·4	5·6	−0·6
*T*O3 II	6·2	−25·1	−40·7	−40·7	−4·3	−2·7	0·2
	6·5	−28·2	−37·9	−41·4	−2·3	−2·2	2·4
*B*O1 I	7·9	−46·0	−52·0	−61·8			−9·4
	8·0	−51·6	−49·2	−60·8			−5·0
*B*O1 II	8·3	−45·8	−49·5	−72·5			19·1
	8·6	−49·8	−47·4	−71·1			10·8
*B*O2 I	5·8	−41·9	−34·6	−19·7			−1·4
	6·7	−37·3	−34·7	−31·8			0·5
*B*O2 II	6·6	−55·9	−43·5	−35·5			6·7
	7·1	−49·0	−41·4	−39·0			5·5
*T*C1 I	5·0	−36·0	−31·9	−34·9	5·0	−2·0	2·1
	5·2	−36·6	−31·4	−30·6	3·7	1·1	3·3
*T*C1 II	4·6	−25·8	−19·3	−45·6	3·2	14·4	9·3
	5·0	−25·6	−22·1	−43·6	2·4	9·8	6·7
*T*C2 I	5·8	−31·7	−40·9	−39·6	−8·2	2·3	−0·6
	6·1	−29·9	−39·6	−40·8	−8·2	2·2	−1·2
*T*C2 II	5·8	−37·1	−43·9	−41·2	−5·0	−2·9	5·3
	6·3	−37·0	−43·3	−43·7	−5·2	−5·2	4·8
*T*C3 I	5·6	−36·2	−39·8	−34·9	0·5	−5·9	−1·0
	5·8	−35·3	−36·3	−34·5	1·7	−5·4	−2·5
*T*C3 II	5·1	−30·9	−35·7	−38·5	2·9	13·3	3·8
	5·6	−31·5	−36·0	−40·1	4·0	12·9	5·5
*B*C1 I	5·4	−32·0	−34·1	−36·3			−1·3
	5·4	−32·9	−31·9	−34·5			−0·0
*B*C1 II	6·6	−46·1	−51·8	−56·8			−0·8
	6·9	−48·6	−50·2	−54·0			−3·8
*B*C2 I	5·5	−52·3	−40·3	−34·8			2·4
	5·7	−47·7	−35·8	−38·9			−0·9
*B*C2 II	5·7	−59·6	−41·2	−27·5			−4·5
	6·3	−56·8	−39·7	−31·1			−5·0

to this point were $B_{\mathrm{Co}}=1$ Å^2, $B_{\mathrm{O}}=4$ Å^2 and $B_{\mathrm{C}}=2$ Å^2 and a cobalt *K*-electron dispersion correction of −2·5 electrons was applied to f_{Co}. A review of the structure analysis up to this stage indicated that the large residual was probably due to poor data. Not only was the photometry of non-integrating Weissenberg spots found to be subject to considerable error, but analytical relations (Phillips, 1954) showed that the Weissenberg distortion corrections which we had used were far too large.

A new set of intensity data was collected with a vacuum-sublimed crystal mounted on a single-crystal orienter, Mo $K\alpha$ radiation, and a proportional counter. The estimated maximum deviation from the mean for these data (as intensities) was 7%. The value of R was immediately reduced from 0·27 to 0·13 by using these new data with the coordinates obtained from the Weissenberg data and a single scaling factor. Increasing the thermal coefficients to $B_{\mathrm{Co}}=3$, $B_{\mathrm{O}}=6$ and $B_{\mathrm{C}}=4$ Å^2 resulted in $R=0·12$. Two cycles of full-

Table 4. *Interatomic distances* (Å) *found in molecules* I *and* II *by least-squares and differential synthesis refinement*

Atoms	Least squares I	Least squares II	Differential synthesis I	Differential synthesis II	Weighted mean*	Average standard deviation $\langle\sigma\rangle$
Co–Co	2·522	2·525	2·522	2·525	2·524	0·002
Co–*T*C1	1·818	1·800	1·784	1·788	1·801	0·016
Co–*T*C2	1·809	1·805	1·799	1·814	1·807	0·013
Co–*T*C3	1·770	1·798	1·780	1·782	1·783	0·013
Co–*B*C1	1·883	1·928	1·904	1·929	1·909	0·012
Co–*B*C2	1·925	1·949	1·910	1·934	1·932	0·012
*T*C1–*T*O1	1·136	1·164	1·183	1·204	1·164	0·022
*T*C2–*T*O2	1·202	1·172	1·200	1·146	1·173	0·018
*T*C3–*T*O3	1·165	1·176	1·156	1·173	1·168	0·018
*B*C1–*B*O1	1·243	1·183	1·213	1·179	1·207	0·019
*B*C2–*B*O2	1·188	1·187	1·233	1·212	1·200	0·018

* Weighted mean = $\frac{1}{3}$ (differential synthesis mean value for molecules I and II, plus twice the least-squares mean value for molecules I and II).

Table 5. *Bond angles* (°) *found in molecules* I *and* II *by least-squares and differential synthesis refinement*

Cobalt–carbon–oxygen angles

Group	Least squares I	Least squares II	Differential synthesis I	Differential synthesis II	Weighted mean*	Average standard deviation $\langle\sigma\rangle$
*T*1	177·9	175·0	176·5	174·1	176·1	1·5
*T*2	175·4	174·2	176·0	175·2	175·1	1·1
*T*3	176·6	177·6	177·5	179·2	177·5	1·1
*B*1	137·8	139·0	138·4	131·7	137·3	1·0
*B*2	139·0	139·5	138·6	139·3	139·2	1·1

Carbon–cobalt–carbon angles

Group	Least squares I	Least squares II	Differential synthesis I	Differential synthesis II	Weighted mean*	Average standard deviation $\langle\sigma\rangle$
*T*1–*T*2	95·5	95·5	95·3	95·0	95·4	0·6
*T*1–*T*3	104·4	107·4	105·1	104·9	105·6	0·7
*T*1–*B*1	155·9	154·0	155·9	156·6	155·4	0·6
*T*1–*B*2	84·1	83·6	84·4	85·6	84·3	0·6
*T*2–*T*3	103·3	101·5	102·9	102·1	102·4	0·6
*T*2–*B*1	88·7	88·5	88·3	88·6	88·5	0·5
*T*2–*B*2	162·7	164·4	162·8	164·7	163·6	0·5
*T*3–*B*1	97·4	96·6	97·3	96·9	97·0	0·6
*T*3–*B*2	93·3	93·4	93·7	92·4	93·2	0·6
*B*1–*B*2	84·7	85·6	84·9	84·9	85·0	0·5
*B*1–*B*2	128·3	127·2	128·2	126·3	127·3	—

* Weighted mean = $\frac{1}{3}$ (differential synthesis mean value for molecules I and II plus twice the least-squares mean value for molecules I and II).

matrix isotropic least-squares refinement (Busing & Levy, 1959) based on

$$\sum_3 w(F_o-F_c)^2$$

with $w=1/F_o^2$ resulted in a final value of $R=0{\cdot}096$ for 1008 observed reflections. The observed and calculated structure factors based on this refinement are listed in Table 1.*

The results of the least-squares refinement were checked by differential synthesis using the final least-squares parameters as the starting parameters. When the atoms showing the largest coordinate changes were recycled, the first cycle shifts either reversed sign or increased but slightly. The final parameters of the

Table 6. *Intermolecular atomic separations*

Oxygen–oxygen	Distance (Å)	Carbon–oxygen	Distance (Å)
*T*O2 I –*B*O2 I	2·971	*T*C3 I–*B*O1 II	3·069
*B*O1 I –*T*O3 II	3·135	*T*C2 I–*B*O2 I	3·143
*T*O3 I –*B*O1 II	3·118	*B*O1 I–*T*C3 II	3·126
*T*O2 I –*T*O3 I	3·163	*B*C1 I–*B*O1 II	3·157
*T*O2 I –*T*O3 II	3·199	*B*O1 I–*B*C1 II	3·298
*T*O1 II–*T*O3 II	3·130	*B*O1 I–*B*C2 II	3·213
*B*O1 I –*B*O2 II	3·281	*B*C2 I *B*O1 II	3·268
*T*O2 I –*T*O1 II	3·344	*T*C3 I–*T*O2 I	3·324
*B*O1 I –*B*O1 II	3·333	*T*O1 I–*T*C2 II	3·390
*T*O1 I –*T*O1 II	3·374		
*T*O1 I –*T*O2 II	3·312		
*T*O2 II–*B*O2 II	3·021		

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* *Note added in proof.*— There are two values in Table 1 for $10F_o$ (042); the correct value in 497.

least-squares and differential synthesis are presented in Table 2. The final peak heights and curvatures obtained from the differential synthesis refinement are given in Table 3. The resulting calculated bond distances and bond angles are listed in Tables 4 and 5 respectively, together with their standard deviations.

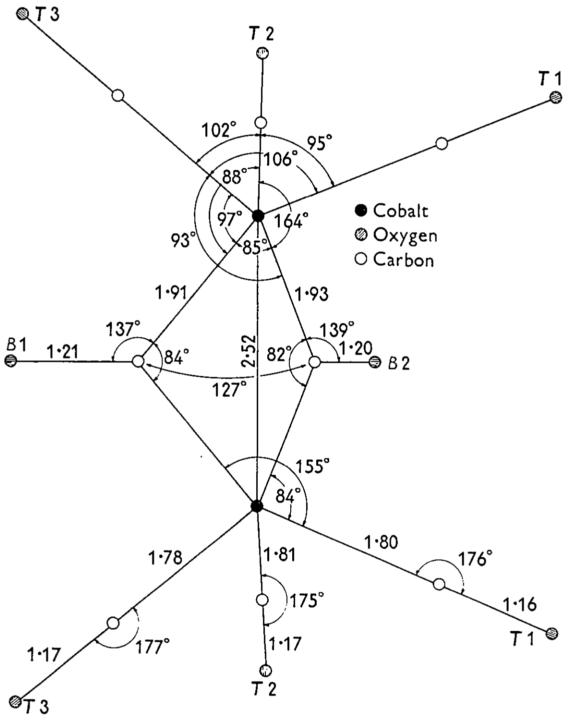

Fig. 1. Dicobalt octacarbonyl intramolecular bond distances and angles based on the final parameters of least-squares and differential synthesis refinement (drawn approximately to scale).

Since no thermal parameter changes were calculated for the differential synthesis, the final bond distances and angles were taken as the weighted mean of the differential synthesis values plus twice the least-square values. Table 6 contains the non-bonded atomic separations.

Fig. 1 is a drawing of the dicobalt octacarbonyl molecule showing most of the bond angles and distances given in Tables 4 and 5. Figs. 2, 3 and 4 are the final coordinate projections down [001], [100] and [010], respectively. The final least-squares parameters were also used to obtain the electron-density map $\varrho(xyz)$ and the difference map $D(xyz)$ in 0·25 Å intervals along [010] using a three-dimensional Fourier synthesis program written for the IBM 704 computer (Sly & Shoemaker, 1959). The electron-density map exhibits all of the atoms of the structure with essentially the same density values as those calculated by the final differential synthesis refinement. There are two apparently spurious areas on the $\varrho(xyz)$ map which are not occupied by atoms. One is an annulus of negative density whose extreme value is $-1{\cdot}5$ e.Å^{-3}. The other is a peak whose maximum value is 3 e.Å^{-3}. Both are located in sections 0/60 and 1/60 along [010] and both have the same x and z coordinates as the Co I and Co II atoms at $y=0{\cdot}832$. These features are apparently due to subsidiary diffraction peaks associated with the strong cobalt peaks, since there is no indication of these deviations in the $D(xyz)$ synthesis. The maximum values of $D(xyz)$ are 0·5 e.Å^{-3} and $-1{\cdot}5$ e.Å^{-3}. These negative areas are found at $y=7/60$, 8/60, 12/60 and 13/60, and are adjacent to the Co I and Co II atoms at $y=0{\cdot}168$ (approximately 10/60) and have the same x and z coordinates as these atoms. These negative areas are presumably the combined result of deviations from isotropic thermal vi-

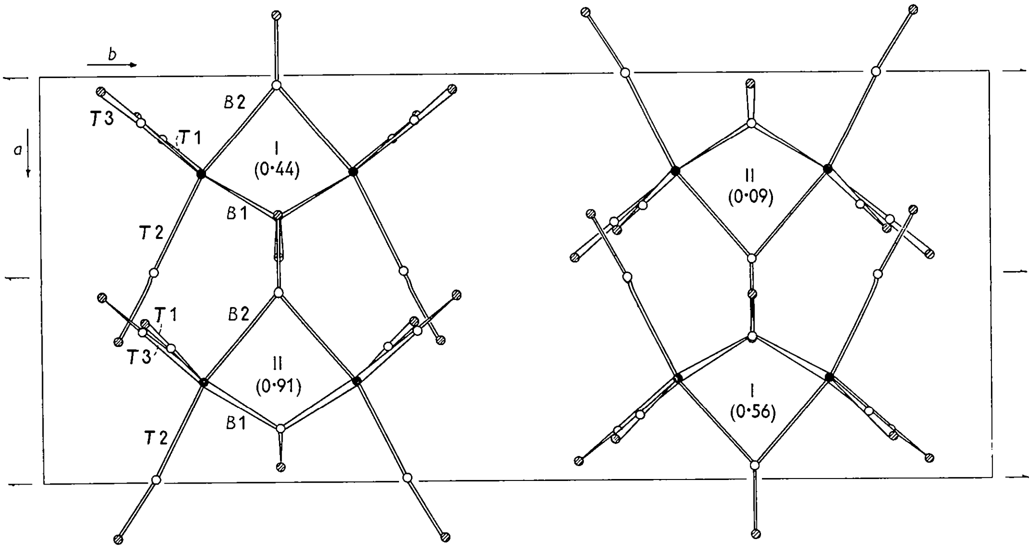

Fig. 2. Diagram of the projection down [001]; numbers in parentheses indicate cobalt z coordinates.
○ cobalt, ▨ oxygen, ● carbon.

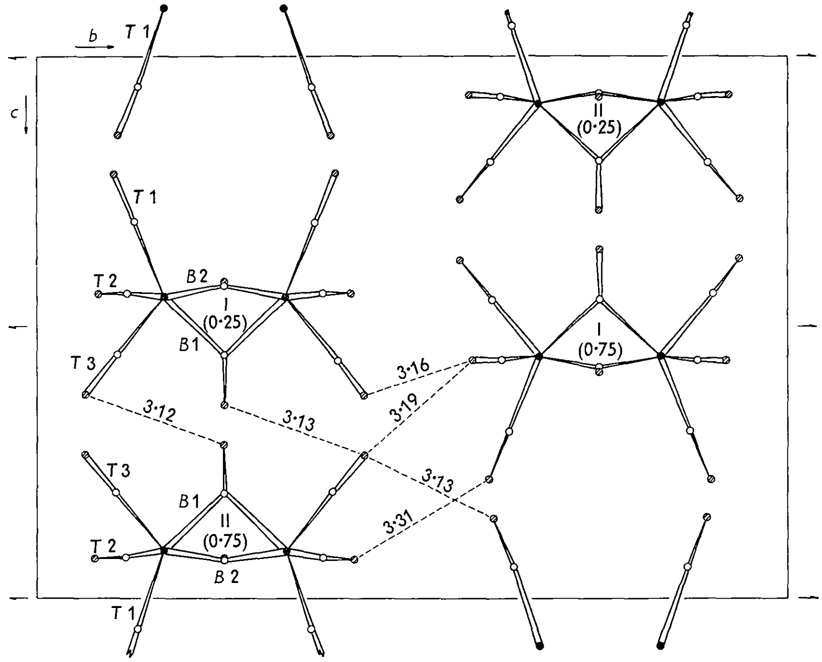

Fig. 3. Diagram of the projection down [100]; numbers in parentheses indicate approximate cobalt x positions. ● cobalt, ▨ oxygen, ○ carbon.

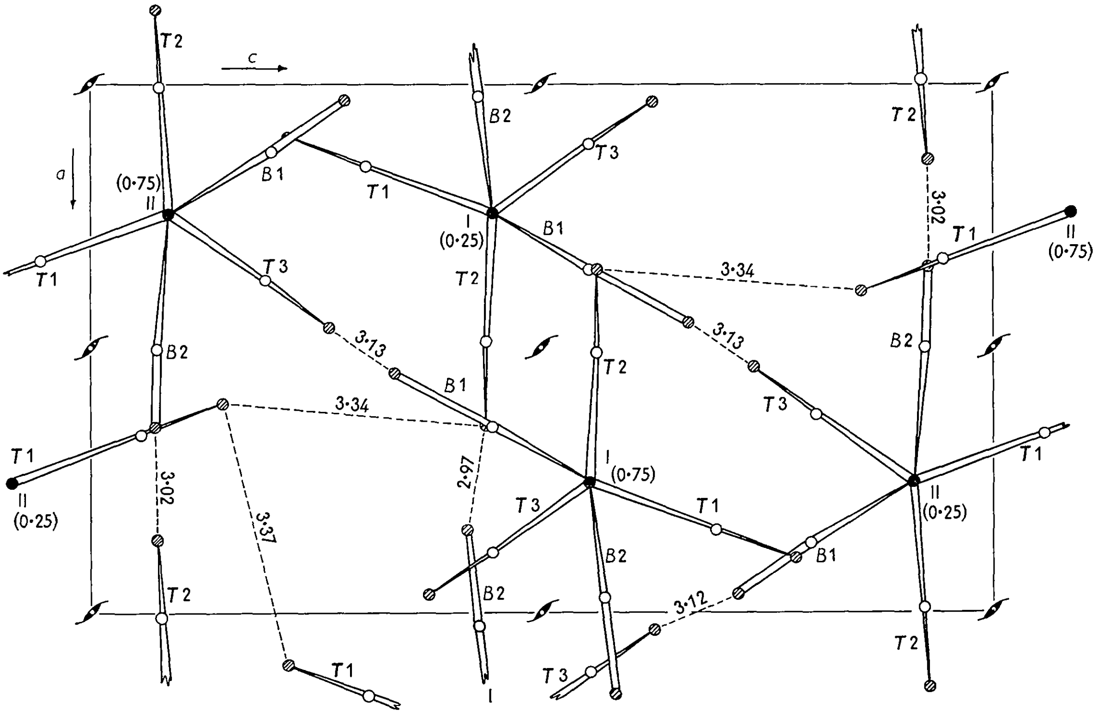

Fig. 4. Diagram of the projection down [010]; numbers in parentheses indicate the position of the molecule along the b axis. ● cobalt, ▨ oxygen, ○ carbon.

bration, *K*-electron dispersion, and small errors in the f_{Co} curve. The other, small, non-zero values of $D(xyz)$ are probably due to anisotropy effects and random errors in the intensity data.

Nomenclature

The nomenclature used in the description of this structure is based on the presence of two crystallographically independent molecules in the unit cell (molecules I and II) each of which contains terminal carbonyls (with designation *T*) and bridge carbonyls (with designation *B*). The terminal groups are designated *T*1, *T*2, and *T*3. The bridge carbonyls are designated *B*1 and *B*2 as they represent an approximate continuation of the *T*1–Co bond or the *T*2–Co bond, respectively. All designations also include the atomic symbol. For example, *T*C1 I is the carbon atom of molecule I in the terminal carbonyl group *T*1.

Description of the structure

The structure of dicobalt octacarbonyl can be described as a distorted $Fe_2(CO)_9$ structure. The extent of the similarity between the two can be seen by comparing the [010] projection of $Co_2(Co)_8$ (Fig. 4) with the [001] projection of $Fe_2(CO)_9$ shown in Fig. 5 together with the $Co_2(CO)_8$ unit cell. The molecular configuration of $Co_2(CO)_8$ is essentially that of iron enneacarbonyl less one bridge carbonyl as predicted by Mills & Robinson (1959). The exact symmetry of the molecule is $C_s=m$, although it approximates *mm* symmetry very closely.

The primary packing units are zigzag chains of molecules which extend along [100] and are located on the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. These chains consist of alternate crystallographically independent (types I and II) molecules whose bridge oxygen atoms form van der Waals contacts between the terminal oxygen atoms *T*O2 and *T*O3 as indicated in the [010] projection (Fig. 4). Were it not for the absence of the third bridge carbonyl, these chains would not be discrete packing units. Instead they would be linked through trigonally distributed van der Waals contacts extending from all of the bridge oxygen atoms to form strongly knit layers (rather than chains) at $y=\frac{1}{4}$ and $\frac{3}{4}$ as in $Fe_2(CO)_9$. Actually these chains in $Co_2(CO)_8$ are loosely bound together into layers at $y=\frac{1}{4}$ and $\frac{3}{4}$ by terminal carbonyl oxygen contacts of length 3·37 and 3·34 Å (Fig. 4). Finally, the layers at $y=\frac{1}{4}$ and $\frac{3}{4}$ are held together by van der Waals contacts between the terminal oxygen atoms in different layers as shown in the [100] projection (Fig. 3). These layers are manifested by the perfect (010) cleavage observed in the $Co_2(CO)_8$ crystals.

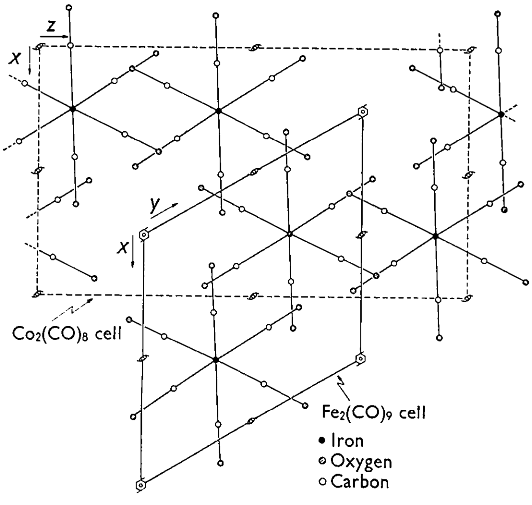

Fig. 5. Projection of the $Fe_2(CO)_9$ structure and the relation of the unit cell to that of $Co_2(CO)_8$.

The electronic configurations about the metal atoms in $Fe_2(CO)_9$ and $Co_2(CO)_8$ can best be described by the diagrams in Fig. 6 which are based on the molecular orbital scheme of Day & Selbin (1962). In $Fe_2(CO)_9$ each Fe atom provides six 3*d* and two 4*s* electrons, the three terminal CO groups contribute six electrons, and the three bridge CO groups contribute three electrons, making a total of 17 electrons for the 3*d*, 4*s*, and 4*p* orbitals of the Fe atom. Because of their symmetry, the *e*, a_1 and t_1 orbitals make available six octahedrally directed covalent σ bonds to the six coordinated CO groups. It is not necessary, and it may actually be undesirable, to consider these six orbitals to have undergone d^2sp^3 hybridization, since there is no reason to believe that the six bonds are all equivalent. The three non-bonding t_2 orbitals on the Fe atom contain only five electrons. Under the trigonal field along the axis of the molecule these non-bonding orbitals split and interact with their counter-

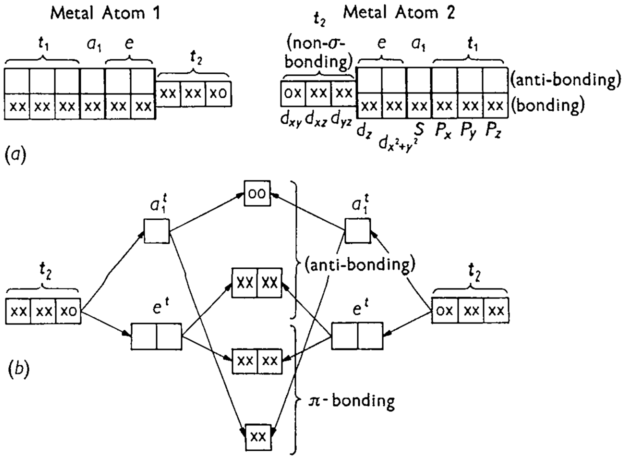

Fig. 6. Proposed electronic configuration for $Fe_2(CO)_9$ and $Co_2(CO)_8$. (*a*) Ligand–metal molecular orbitals around the metal atoms prior to t_2 orbital splitting. (*b*) Splitting of the t_2, σ-type, non-bonding orbitals and their subsequent interaction.

part from the other Fe atom. This interaction gives rise to three bonding orbitals and three antibonding orbitals which are of σ symmetry with respect to the trigonal axis, but of π symmetry with respect to the original rectangular coordinates. The lowest is the orbital directed along the trigonal axis, and it leads to a bond of considerable strength between the two Fe atoms. The observed diamagnetism is thereby explained. The two remaining bonding orbitals contribute to the dative π bonding which is generally assumed to be responsible for the observed shortening of the terminal metal–carbon distances in the metal carbonyls. A somewhat similar proposal for $Fe_2(CO)_9$ by Dunitz & Orgel (1953) has recently come to our attention.

The same diagram (Fig. 6) can be used to describe the $Co_2(CO)_8$ molecule. Each Co atom provides seven $3d$ and two $4s$ electrons, the three terminal CO groups contribute six electrons, and the two bridge CO groups contribute two electrons. Again we have 17 electrons for the $3d$, $4s$, and $4p$ orbitals of the Co atom, and the same six octahedral covalent bonds are available. The five, coordinated, CO groups are thereby σ-bonded to the Co, and the sixth position (the third bridge position) is to be considered as occupied by a *virtual* atom. The orbitals at this position will extend in much the same fashion as if there were an atom there furnishing orbitals to form the bond, but the overlap will be much smaller. The three non-bonding t_2 orbitals again contain only five electrons, which, because of the approximate trigonal symmetry, are expected to split and interact with their counterpart from the other Co atom. This interaction will give rise to the same metal–metal bonding as in $Fe_2(CO)_9$, and $Co_2(CO)_8$ will be diamagnetic as observed.

Published bond distances and angles show that those metal carbonyls with carbonyl bridges are very similar in the bridge region (*e.g.* Mills, 1958; Sly, 1959; Mills, 1961; Hock & Mills, 1961), while the non-bridged metal carbonyls exhibit metal–metal separations which are variable and inexplicably large (Dahl, Ishishi & Rundle, 1957; Wilson & Shoemaker, 1957). It thus appears that the bridge carbonyl groups may determine the metal–metal separation as well as the other bond distances and angles in the bridge region, and that these bridge carbonyl distances and angles are as characteristic as those in the terminal carbonyl region.

Most of the bond angles and distances in $Co_2(CO)_8$ are typical of those found in other metal carbonyls with the possible exception of the cobalt–cobalt separation of 2·52 Å, which is 0·03 Å to 0·06 Å longer than that observed in any other bridged metal carbonyls. While we believe the carbonyl bridges are the determinative structural linkages between the two halves of the molecule, which should therefore result in characteristically uniform metal–metal distances, it is not surprising that the metal–metal separation should change slightly with only two bridge groups present.

The mean terminal carbon–oxygen distance of 1·17 Å is roughly midway between the observed extreme values of 1·12 and 1·26 Å. It is the same carbon–oxygen distance observed in ketene (Brown & Livingstone, 1952) and carbon dioxide (Allen & Sutton, 1950). The bridge metal–carbon distance has a mean value of 1·92 Å as compared with 1·8 Å in $Fe_2(CO)_9$ (Powell & Ewens, 1939) and 1·82 Å in $Fe_2(CO)_4(C_5H_5)_2$ (Mills, 1958). The $Fe_2(CO)_9$ value is probably not reliable since the bridge metal–carbon distance was reported as being shorter than the terminal metal–carbon distance, which is probably incorrect. The distance in $Fe_2(CO)_4(C_5H_5)_2$ is reliable for comparative purposes and the structure has but two bridges, however the conjugated systems in the terminal region may affect the bridge metal–carbon distance. It seems quite possible, for example, that the bridge area conjugation is affecting the terminal area in $Co_2(CO)_6C_2(C_6H_5)_2$ considering the rather long terminal carbon–oxygen distances of mean value 1·23 Å which were found (Sly, 1959). Perhaps the best direct comparison possible is with the values found for $Co_2(CO)_7C_4H_2O_2$ (Mills, 1961) whose mean bridge metal–carbon distance is 1·92 Å, which is the value found in $Co_2(CO)_8$ and also that calculated from covalent radii (Pauling, 1947).

The terminal metal–carbon–oxygen angles in $Co_2(CO)_8$ show departures from linearity in the range of 3 to 5°, which are typical in metal carbonyl determinations. Although three standard deviations (3σ) amount to about 3° for these angles, the departures observed are probably not real. The only established example of a non-linear terminal carbonyl group is in the unusual structure of $Fe_2(CO)_6C_4(OH)_2(CH_3)_2$ (Hock & Mills, 1961), in which a terminal group appears to serve also in a bridging capacity.

The planarity of the Co–C–C–C–C group is fairly good considering the distortion to be expected in the $Co_2(CO)_8$ molecule. For example, choosing the final least-squares coordinates for the *T*C1 I, *B*C1 I, and *B*C2 I atoms as the points defining a plane, the equation of which is $-0{\cdot}947\ x-1{\cdot}556\ y+1{\cdot}486\ z=1$, we find that the *T*C2 I and Co I atoms are only 0·2 and 0·4 Å, respectively, out of the plane. We conclude that while there is some departure from a strict octahedral configuration, it is not excessive and that the $Co_2(CO)_8$ molecular structure is undoubtedly a variation of the $Fe_2(CO)_9$ structure which in turn is definitely based on an octahedral configuration.

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The Crystal Structure of Boron Trifluoride Dihydrate

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The crystal structure of boron trifluoride dihydrate has been determined at 3 °C by X-ray diffraction. The crystals belong to the monoclinic space group $P2_1/c$ and have cell dimensions

$$a = 5{\cdot}606,\ b = 7{\cdot}438,\ c = 8{\cdot}683\ \text{Å};\ \beta = 90{\cdot}45^\circ.$$

$BF_3.2H_2O$ appears to have a structure with one water molecule bonded to boron to form the molecular addition compound $F_3B.OH_2$; the other water molecule links these together by means of hydrogen bonds. However, the ionic formulation $[H_3O]^+[BF_3OH]^-$ cannot be entirely excluded by the diffraction evidence.

Introduction

The early observation by Klinkenberg & Ketelaar (1935) that the X-ray diffraction pattern of $BF_3.2H_2O$ is very similar to those of NH_4BF_4 and NH_4ClO_4 suggested that the former compound is isomorphous with the latter compounds, and so is probably a hydronium salt in the solid. The presence of H_3O^+ and BF_3OH^- in the liquid was indicated by the conductometric measurements of Greenwood & Martin (1951). It would then be interesting to compare the pattern of hydrogen bonding here with those in other hydronium salts such as H_3OCl (Yoon & Carpenter, 1959) and H_3OClO_4 (Lee & Carpenter, 1959). On the other hand, Ford & Richards (1956) concluded from nuclear magnetic resonance studies that in slowly crystallized boron trifluoride dihydrate the water molecules are present in molecular complexes. The present structure determination was undertaken to ascertain the true nature of this substance and to investigate the hydrogen bonding pattern. Additional details of this work are presented in a thesis by one of us (Bang, 1963).

Experimental

Boron trifluoride dihydrate, prepared by introducing boron trifluoride gas into water and subsequent fractional crystallization, was sealed in Pyrex glass