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The Crystal and Molecular Structures of Bis(2,4-pentanedionato)chromium

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Bis(2,4-pentanedionato)chromium(II) has been prepared in crystalline form by slow sublimation in a sealed tube at 105–110 °C. There are two equivalent molecules in the monoclinic unit cell, space group $P2_1/n$, *with the following dimensions:* $a = 11.445(4)$, $b = 4.748(1)$, $c = 10.325(3)$ Å, $\beta = 91.60(3)^\circ$, $V = 560.8(5)$ Å^3, $d_{calcd} = 1.48$ g/cm^3. *The chromium atom lies on an inversion center and has planar coordination by four oxygen atoms at a mean Cr–O distance of 1.98Å. There are weak interactions (3.05Å) with carbon atoms of ligands in adjacent molecules to complete a severely tetragonally distorted octahedral coordination sphere about chromium. The chromium compound is isomorphous with bis(2,4-pentanedionato)copper(II).*

Introduction

The initial publication of the synthesis of bis(2,4-pentanedionato)chromium(II), $Cr(C_5H_7O_2)_2$, by Costa and Puxeddu [1] mentioned that the substance has low solubility and a magnetic moment of 4.99 B.M., consistent with a high spin d^4 metal ion. On the basis of these data, it has been suggested [2, 3] that the compound is polymeric, presumably with distorted octahedral coordination about chromium, attained through bridging acetylacetonato oxygen atoms. In the absence of direct structural data on $Cr(C_5H_7O_2)_2$ itself, the presumption was not unreasonable in view of the polymeric structures known for $[Co(C_5H_7O_2)_2]_4$ [4], $[Ni(C_5H_7O_2)_2]_3$ [5] and $[Zn(C_5H_7O_2)_2]_3$ [6].

We became interested in the structure of this compound in connection with our studies of carboxylato-bridged Cr(II) compounds [7, 8], and we have determined its crystal and molecular structures by conventional X-ray crystallographic methods.

Experimental

Synthesis of $Cr(C_5H_7O_2)_2$

This was prepared *via* chromium(II) acetate by a standard method [9]. A small portion of the light yellow–brown product was transferred in an inert-atmosphere box to a 12 X 70 mm glass tube. The sample was dried at 100 °C under vacuum for 6 hours and the tube was sealed under vacuum. Sublimation at 105–110 °C for 40 hours in a small muffle furnace yielded a sublimate composed of an approximately 2:1 mixture of separate purple and light brown crystals. The sublimation tube was opened in the inert-atmosphere box and the crystals were immediately covered with heavy, degassed mineral oil. Specimens of each crystal type were coated with epoxy cement and mounted in glass capillaries. The purple crystals were identified as $Cr(C_5H_7O_2)_3$ by a cell constant determination, which gave constants identical within experimental error limits to published values [10].

X-ray Data Collection for $Cr(C_5H_7O_2)_2$

The crystal selected was a needle with dimensions 0.15 X 0.15 X 0.6 mm. Data were collected on a Syntex P$\bar{1}$ automated diffractometer using Mo Kα radiation monochromatized with a graphite crystal monochromator in the incident beam. The automatic centering and indexing procedures followed have been described [11]. The monoclinic cell parameters are $a = 11.445(4)$, $b = 4.748(1)$, $c = 10.325(3)$Å $\beta = 91.60(3)^\circ$, V = 560.8(5)Å^3, $d_{calcd} = 1.48$ g/cm^3 for Z = 2 and a formula weight of 250.22.

A total of 1234 unique reflections with $0^\circ < 2\theta \leqslant 55^\circ$ were collected using the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from 2θ (MoKα_1) −1.0° to 2θ (MoKα_2) + 1.0°. Intensities of three standard reflections measured after every 40 reflections showed no significant variation during data collection. Lorentz and polarization corrections were applied [12] but absorption corrections were deemed unnecessary (absorption coefficient = 10.53).

Solution and Refinement of the Structure [12]

The structure was solved in the space group $P2_1/n$ and refined using only those 740 reflections for which $F_o^2 > 3\sigma(F_o^2)$. The positions of the chromium atom and one oxygen atom were determined using a three-dimensional Patterson function. After refining these positions by least-squares, a difference Fourier map revealed the positions of the remaining oxygen atom and three of the five carbon atoms. The remaining carbon atoms were found by successive refinements and Fourier difference maps. Isotropic refine-

TABLE I. Values of $10F_0$ and $10F_c$ for $Cr(acac)_2$.

H	K	L	FOBS	FCALC
0	0	2	537	544
0	0	4	58	111
0	0	6	370	349
0	0	10	162	171
0	0	12	126	142
0	1	1	65	68
0	1	2	151	136
0	1	3	261	273
0	1	4	461	428
0	1	5	345	354
0	1	7	195	195
0	1	8	54	63
0	1	11	58	49
0	1	13	68	69
0	2	0	394	394
0	2	2	308	301
0	2	3	59	60
0	2	4	261	261
0	2	5	101	95
0	2	6	185	185
0	2	8	186	194
0	2	9	57	41
0	2	10	196	200
0	3	1	45	50
0	3	3	249	255
0	3	5	220	223
0	3	6	72	74
0	3	7	163	163
0	3	8	64	61
0	3	9	104	100
0	3	10	63	67
0	4	0	245	235
0	4	2	151	156
0	4	4	56	63
0	4	5	60	62
0	4	6	86	84
0	4	8	68	72
0	5	1	171	181
0	5	3	99	92
0	5	4	59	62
0	5	5	111	112
0	5	7	64	65
1	0	-13	80	84
1	0	-11	137	139
1	0	-9	64	92
1	0	-7	187	208
1	0	-5	50	76
1	0	3	558	500
1	0	5	574	539
1	0	7	227	217
1	0	9	92	98
1	0	11	73	63
1	0	13	62	57
1	1	-12	72	74
1	1	-8	214	215
1	1	-7	94	96
1	1	-6	170	172
1	1	-5	292	281
1	1	-4	362	350
1	1	-3	228	222
1	1	-2	554	496
1	1	-1	83	76
1	1	0	73	89
1	1	1	309	346
1	1	2	518	521
1	1	3	79	83
1	1	4	284	266
1	1	5	144	152
1	1	6	84	96
1	1	8	151	155
1	1	10	62	51
1	1	12	63	64
1	2	-11	60	68
1	2	-9	187	194
1	2	-7	165	171
1	2	-5	234	219
1	2	-4	181	167
1	2	-3	468	471
1	2	-2	50	49
1	2	-1	254	276
1	2	0	97	76
1	2	1	70	78
1	2	2	48	45
1	2	3	336	329
1	2	4	67	81
1	2	5	188	189
1	2	6	182	190
1	2	7	158	152
1	2	9	228	234
1	2	11	63	70
1	3	-10	60	61
1	3	-8	149	145
1	3	-7	96	90
1	3	-6	161	158
1	3	-5	65	65
1	3	-4	294	298
1	3	-2	259	255
1	3	1	97	113
1	3	2	196	202
1	3	4	189	180
1	3	5	217	226
1	3	6	77	76
1	3	8	115	133
1	3	10	110	110
1	4	-9	66	75
1	4	-8	59	56
1	4	-7	91	85
1	4	-5	86	89
1	4	-4	203	210
1	4	-3	93	100
1	4	-1	189	191
1	4	1	196	197
1	4	2	89	86
1	4	3	112	105
1	4	4	59	69
1	4	5	122	121
1	4	6	77	68
1	4	7	97	101
1	5	-6	92	95
1	5	-5	85	69
1	5	-2	60	59
1	5	0	194	198
1	5	2	116	117
1	5	4	125	126
1	5	6	119	115
1	6	-3	74	81
1	6	1	72	56
2	0	-12	137	138
2	0	-10	93	89
2	0	-6	358	364
2	0	-4	102	73
2	0	-2	86	58
2	0	0	527	537
2	0	2	216	166
2	0	4	401	388
2	0	6	587	599
2	0	8	106	105
2	1	-13	61	49
2	1	-11	121	127
2	1	-9	239	237
2	1	-8	155	157
2	1	-7	229	224
2	1	-6	93	83
2	1	-5	280	276
2	1	-4	266	209
2	1	-3	122	184
2	1	-2	86	92
2	1	-1	376	362
2	1	0	325	328
2	1	2	482	417
2	1	3	418	419
2	1	4	156	155
2	1	5	187	178
2	1	7	197	194
2	1	9	59	54
2	1	11	124	130
2	1	13	79	72
2	2	-10	82	78
2	2	-8	65	34
2	2	-7	50	42
2	2	-6	180	179
2	2	-5	107	93
2	2	-4	486	491
2	2	-2	459	442
2	2	-1	104	100
2	2	0	106	105
2	2	1	75	66
2	2	2	54	51
2	2	3	44	64
2	2	4	161	174
2	2	5	189	187
2	2	6	139	148
2	2	8	162	157
2	2	10	98	102
2	2	11	74	67
2	3	-9	126	120
2	3	-7	132	127
2	3	-5	171	181
2	3	-4	101	94
2	3	-3	261	265
2	3	-1	199	209
2	3	1	283	279
2	3	2	80	61
2	3	3	229	221
2	3	6	103	105
2	3	7	75	72
2	3	9	99	105
2	3	11	78	84
2	4	-9	59	57
2	4	-8	88	82
2	4	-7	58	63
2	4	-6	123	126
2	4	-5	83	79
2	4	-4	122	120
2	4	-2	136	145
2	4	0	164	177
2	4	1	141	142
2	4	2	126	139
2	4	4	129	129
2	4	5	57	50
2	4	6	158	160
2	4	8	88	86
2	5	-7	75	85
2	5	-4	60	62
2	5	-1	95	98
2	5	1	94	94
2	5	3	87	90
2	5	5	118	117
2	6	-2	89	92
2	6	2	83	93
3	0	-13	135	136
3	0	-11	128	117
3	0	-7	336	340
3	0	-5	189	195
3	0	-1	535	461
3	0	1	312	271
3	0	3	124	110
3	0	5	427	429
3	0	7	132	142
3	0	9	109	109
3	1	-12	61	54
3	1	-11	58	73
3	1	-10	134	132
3	1	-8	296	304
3	1	-7	143	142
3	1	-6	243	255
3	1	-4	216	212
3	1	-3	377	323
3	1	-2	316	315
3	1	-1	96	105
3	1	0	440	459
3	1	1	488	431
3	1	2	545	548
3	1	3	84	80
3	1	4	348	351
3	1	6	270	257
3	1	8	192	184
3	1	9	58	52
3	1	10	131	121
3	1	12	71	68
3	2	-12	58	49
3	2	-7	58	61
3	2	-5	170	161
3	2	-3	511	514
3	2	-2	48	45
3	2	-1	390	384
3	2	1	71	78
3	2	2	47	31
3	2	3	314	314
3	2	5	82	88
3	2	9	129	131
3	3	-10	83	85
3	3	-8	131	130
3	3	-6	92	86
3	3	-4	199	205
3	3	-3	130	130
3	3	-2	265	274
3	3	-1	57	59
3	3	0	233	235
3	3	1	91	74
3	3	2	289	272
3	3	3	118	111
3	3	4	157	145
3	3	5	73	73
3	3	6	61	49
3	3	7	84	95
3	3	8	100	93
3	3	10	70	86
3	3	11	73	79
3	4	-9	79	66
3	4	-7	107	109
3	4	-6	53	49
3	4	-5	143	143
3	4	-3	114	111
3	4	-2	124	131
3	4	-1	134	132
3	4	0	67	69
3	4	1	152	159
3	4	2	128	136
3	4	3	114	116
3	4	5	158	163
3	4	7	130	122
3	5	-6	98	101
3	5	-3	83	82
3	5	0	95	90
3	5	4	72	69
3	5	6	82	90
3	6	1	99	99
4	0	-12	108	95
4	0	-10	109	113
4	0	-8	254	263
4	0	-6	493	497
4	0	-4	162	178
4	0	0	340	327
4	0	2	235	217
4	0	4	241	249
4	0	6	223	226
4	0	8	65	75
4	0	12	87	94
4	1	-11	75	85
4	1	-10	62	62
4	1	-9	145	134
4	1	-7	63	59
4	1	-5	316	330
4	1	-4	122	105
4	1	-3	394	371
4	1	-2	461	436
4	1	-1	265	239
4	1	0	59	69
4	1	1	390	395
4	1	2	171	169
4	1	5	211	210
4	1	7	318	332
4	1	9	104	101
4	1	10	58	55
4	1	11	93	87
4	2	-12	67	52
4	2	-10	127	123
4	2	-8	123	118
4	2	-6	76	84
4	2	-4	238	237
4	2	-3	162	142
4	2	-2	266	255
4	2	0	228	233
4	2	1	82	73
4	2	2	525	515
4	2	3	126	125
4	2	4	299	296
4	2	7	109	110
4	2	8	58	53
4	3	-11	66	78
4	3	-9	96	96
4	3	-5	129	118
4	3	-4	83	76
4	3	-3	263	266
4	3	-1	221	227
4	3	0	61	60
4	3	1	252	245
4	3	2	134	129
4	3	3	172	178
4	3	5	88	83
4	3	6	90	95
4	3	7	123	117
4	3	8	84	73
4	3	9	87	85
4	4	-8	82	84
4	4	-6	148	152
4	4	-4	100	103
4	4	-3	191	191
4	4	-2	72	69
4	4	-1	62	68
4	4	0	132	127
4	4	2	126	116
4	4	4	118	113
4	4	6	122	122
4	4	8	62	63
4	5	-7	129	124
4	5	-5	94	86
4	5	-3	57	63
4	5	-2	65	71
4	5	-1	127	126
4	5	5	80	76
4	5	7	62	55
5	0	-11	63	34
5	0	-9	86	79
5	0	-7	515	531
5	0	-5	388	384
5	0	-3	205	208
5	0	-1	544	544
5	0	1	163	165
5	0	3	255	267
5	0	5	262	281
5	0	7	106	96
5	0	9	140	134
5	0	11	92	100
5	1	-12	100	101
5	1	-11	80	76
5	1	-10	84	81
5	1	-8	51	36
5	1	-6	129	132
5	1	-5	150	149
5	1	-4	201	204
5	1	-3	183	198
5	1	-2	323	328
5	1	-1	223	214
5	1	0	361	353
5	1	2	54	36
5	1	3	120	123
5	1	4	85	85
5	1	6	188	196
5	1	7	60	75
5	1	8	81	70
5	1	10	97	91
5	2	-11	78	69
5	2	-9	151	155
5	2	-7	179	191
5	2	-5	108	107
5	2	-3	211	204
5	2	-2	177	168
5	2	-1	173	177
5	2	1	265	266
5	2	2	88	96
5	2	3	512	493
5	2	5	182	180
5	2	6	69	76
5	2	7	62	48
5	2	9	112	111
5	3	-10	101	102
5	3	-8	66	67
5	3	-4	150	144
5	3	-2	202	197
5	3	-1	156	159
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5	3	1	64	76
5	3	2	191	195
5	3	3	117	132
5	3	4	158	164
5	3	6	115	110
5	3	7	105	98
5	3	8	68	76
5	4	-7	111	113
5	4	-5	129	130
5	4	-3	78	74
5	4	-1	107	105
5	4	1	123	118
5	4	5	80	83
5	4	7	67	75
5	5	-6	121	114
5	5	-4	92	99
5	5	-2	128	131
5	5	0	96	103
5	5	3	65	57
5	5	6	80	73
6	0	-8	149	145
6	0	-6	213	213
6	0	-4	288	305
6	0	-2	585	539
6	0	0	476	452
6	0	2	240	251
6	0	4	44	41
6	0	6	137	128
6	0	8	187	196
6	0	10	86	87
6	0	12	94	89
6	1	-11	86	81
6	1	-9	128	117
6	1	-7	107	107
6	1	-6	119	117
6	1	-5	260	258
6	1	-4	94	96
6	1	-3	181	181
6	1	-2	52	55
6	1	-1	123	127
6	1	1	256	247
6	1	2	58	58
6	1	3	115	127
6	1	4	87	90
6	1	5	172	167
6	1	7	88	84
6	1	8	79	77
6	2	-11	58	48
6	2	-10	133	143
6	2	-8	162	160
6	2	-4	196	203
6	2	-3	57	40
6	2	-2	207	207
6	2	-1	218	216
6	2	0	97	97
6	2	1	48	54
6	2	2	362	350
6	2	4	183	185
6	2	5	63	58
6	2	6	71	82
6	2	8	196	190
6	2	10	68	70
6	3	-9	113	113
6	3	-7	87	79
6	3	-5	126	131
6	3	-4	77	71
6	3	-3	138	132
6	3	-2	204	205
6	3	0	74	71
6	3	1	128	129
6	3	3	210	213
6	3	4	75	74
6	3	5	146	143
6	3	6	72	65
6	3	7	100	91
6	4	-8	61	59
6	4	-6	108	108
6	4	-5	77	80
6	4	-4	95	87
6	4	-2	114	119
6	4	-1	60	67
6	4	0	170	169
6	4	2	69	62
6	4	6	71	58
6	4	7	64	43
6	5	-5	90	85
6	5	-3	100	102
6	5	-1	123	131
6	5	1	68	63
6	5	3	77	67
6	5	5	70	71
7	0	-11	85	84
7	0	-7	84	84
7	0	-3	170	171
7	0	-1	551	557
7	0	1	311	318
7	0	3	62	50
7	0	5	71	77
7	0	7	81	93
7	0	9	65	68
7	1	-10	59	53
7	1	-8	103	100
7	1	-6	321	335
7	1	-5	171	168
7	1	-4	221	212
7	1	-2	139	149
7	1	0	275	280
7	1	1	58	50
7	1	2	117	111
7	1	3	74	83
7	1	4	265	261
7	1	5	57	46
7	1	6	176	168
7	1	10	63	65
7	2	-11	92	99
7	2	-9	152	151
7	2	-7	89	82
7	2	-5	73	64
7	2	-4	68	76
7	2	-3	180	186
7	2	-2	110	119
7	2	-1	121	116
7	2	1	132	130
7	2	2	48	50
7	2	3	149	164
7	2	4	163	179
7	2	5	78	69
7	2	7	127	124
7	2	9	124	115
7	3	-10	73	66
7	3	-8	94	103
7	3	-6	157	154
7	3	-5	59	55
7	3	-4	160	164
7	3	-2	72	69
7	3	-1	75	64
7	3	2	118	120
7	3	3	88	81
7	3	4	153	147
7	3	5	88	83
7	3	6	104	99
7	3	8	80	63
7	4	-7	83	77
7	4	-6	75	66
7	4	-5	86	81
7	4	-3	88	88
7	4	-2	59	67
7	4	-1	171	167
7	4	1	127	140
7	4	4	63	48
7	4	5	66	67
7	5	-2	100	93
7	5	0	82	80
7	5	2	80	71
8	0	-8	107	111
8	0	-2	176	175
8	0	0	162	165
8	0	2	206	203
8	0	4	88	88
8	0	6	105	103
8	0	8	68	58
8	1	-11	75	62
8	1	-9	86	87
8	1	-8	69	70
8	1	-7	152	147
8	1	-6	69	53
8	1	-5	174	174
8	1	-4	64	61
8	1	-3	177	190
8	1	-1	283	280
8	1	1	234	240
8	1	3	208	209
8	1	4	62	52
8	1	5	132	145
8	1	7	63	59
8	1	9	94	92
8	2	-10	97	101
8	2	-8	136	130
8	2	-6	60	64
8	2	-4	222	227
8	2	-2	143	131
8	2	-1	60	53
8	2	1	54	62
8	2	2	131	135
8	2	3	70	81
8	2	4	76	71
8	2	5	61	65
8	2	6	55	65
8	2	8	125	118
8	3	-9	92	89
8	3	-7	94	96
8	3	-5	137	135
8	3	-4	80	86
8	3	-3	141	145
8	3	-1	72	83
8	3	0	128	126
8	3	1	91	98
8	3	3	115	113
8	3	4	118	127
8	3	9	67	78
9	4	-6	87	86
8	4	-4	71	74
8	4	-2	102	105
8	4	0	137	136
8	4	2	65	67
8	4	4	79	87
8	4	6	84	87
8	5	-1	81	70
8	5	1	77	75
9	0	-7	123	122
9	0	-5	159	167
9	0	-3	80	77
9	0	-1	93	98
9	0	1	128	130
9	0	3	70	69
9	0	5	187	189
9	0	7	115	113
9	1	-10	111	100
9	1	-9	61	66
9	1	-8	89	88
9	1	-7	71	75
9	1	-6	131	127
9	1	-2	132	138
9	1	0	303	304
9	1	1	75	76
9	1	2	144	141
9	1	4	149	144
9	1	5	74	77
9	1	6	72	79
9	1	10	97	96
9	2	-9	64	57
9	2	-7	76	63
9	2	-5	216	218
9	2	-3	241	241
9	2	0	99	104
9	2	1	65	59
9	2	2	63	48
9	2	3	64	65
9	2	5	63	58
9	2	7	91	85
9	3	-8	79	79
9	3	-6	75	86
9	3	-5	73	60
9	3	-4	108	106
9	3	-2	113	111
9	3	-1	81	81
9	3	0	131	122
9	3	1	112	109
9	3	2	114	113
9	3	4	62	44
9	4	-5	64	67
9	4	-1	97	96
9	4	1	66	71
9	4	5	88	88
10	0	-8	143	139
10	0	-6	135	139
10	0	-4	128	130
10	0	-2	113	118
10	0	0	120	120
10	0	2	127	138
10	0	4	124	131
10	0	6	130	135
10	1	-9	62	79
10	1	-7	133	125
10	1	-3	65	63
10	1	-2	56	47
10	1	-1	136	136
10	1	2	53	57
10	1	3	119	111
10	1	5	63	73
10	1	9	85	82
10	2	-9	62	43
10	2	-8	67	52
10	2	-6	71	63
10	2	-4	209	212
10	2	-2	161	159
10	2	0	88	90
10	2	2	150	152
10	2	4	66	65
10	3	-5	78	75
10	3	-4	57	61
10	3	-3	121	124
10	3	-1	107	102
10	3	0	66	66
10	3	1	89	84
10	3	3	91	74
10	3	6	71	71
10	4	0	61	69
10	4	1	67	61
10	4	4	70	67
11	0	-9	103	113
11	0	-7	149	147
11	0	-5	151	149
11	0	-1	98	95
11	0	1	190	198
11	0	3	73	70
11	0	5	135	128
11	0	7	64	82
11	1	-6	92	91
11	1	-4	98	98
11	1	-3	53	50
11	1	-2	115	120
11	1	-1	58	49
11	1	1	57	65
11	2	-8	61	47
11	2	-5	102	98
11	2	-3	87	89
11	2	-2	57	50
11	2	-1	79	77
11	2	1	194	194
11	2	3	123	119
11	3	-4	99	99
11	3	-2	108	104
11	3	0	72	74
11	3	2	67	69
11	3	5	65	52
12	0	-8	87	105
12	0	-6	127	137
12	0	0	108	111
12	0	4	65	57
12	0	6	77	72
12	1	-7	94	85
12	1	-5	65	59
12	1	-3	130	139
12	1	-1	123	117
12	1	3	76	77
12	1	6	59	39

TABLE II. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations.

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.0[b]	0.0	0.0	0.00602(8)	0.0267(4)	0.00652(9)	−0.0051(5)	0.0031(1)	−0.0021(6)
O(1)	0.1364(3)	0.2084(8)	−0.0656(3)	0.0065(3)	0.029(2)	0.0079(4)	−0.003(1)	0.0043(5)	−0.001(1)
O(2)	0.0102(3)	0.2157(8)	0.1640(3)	0.0070(3)	0.032(2)	0.0065(3)	−0.005(1)	0.0033(5)	−0.003(1)
C(1)	0.2832(5)	0.552(1)	−0.0896(6)	0.0080(5)	0.050(4)	0.0089(5)	−0.014(2)	0.0065(8)	−0.003(2)
C(2)	0.1876(5)	0.420(1)	−0.0128(5)	0.0049(4)	0.029(2)	0.0079(5)	−0.001(2)	−0.0001(7)	0.002(2)
C(3)	0.1596(4)	0.536(1)	0.1071(5)	0.0058(4)	0.037(3)	0.0061(4)	−0.001(2)	0.0001(7)	−0.004(2)
C(4)	0.0758(4)	0.426(1)	0.1888(5)	0.0048(4)	0.029(2)	0.0071(5)	0.004(2)	−0.0015(7)	0.001(2)
C(5)	0.0563(5)	0.567(1)	0.3196(5)	0.0082(5)	0.047(3)	0.0059(4)	−0.003(2)	0.0014(8)	−0.009(2)

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] The chromium position is fixed by the symmetry of the space group.

TABLE III. Interatomic Distances and Angles.

Intramolecular Distances (Å)		Bond Angles (°)	
Cr–O(1)	1.984(3)	O(1)–Cr–O(1′)	90.3(1)
Cr–O(2)	1.979(3)	O(1)–Cr–O(2′)	89.7(1)
O(1)–C(2)	1.276(5)	Cr–O(1)–C(2)	127.0(3)
O(2)–C(4)	1.272(5)	Cr–O(2)–C(4)	126.8(3)
C(2)–C(3)	1.401(6)	O(1)–C(2)–C(3)	125.1(4)
C(4)–C(3)	1.397(6)	O(2)–C(4)–C(3)	125.7(4)
C(2)–C(1)	1.508(6)	O(1)–C(2)–C(1)	115.8(4)
C(4)–C(5)	1.528(6)	O(2)–C(4)–C(5)	114.9(4)
		C(2)–C(3)–C(4)	124.3(4)
Intermolecular Distance[a]		C(3)–C(2)–C(1)	119.1(4)
Cr–C(3″)	3.048(5)	C(3)–C(4)–C(5)	119.4(4)
		Intermolecular angles[a]	
Cr–C(3″)–C(2″)	96.6(3)	O(1)–Cr–C(3″)	90.8(1)
Cr–C(3″)–C(4″)	94.3(3)	O(2)–Cr–C(3″)	92.5(1)

[a] The atom C(3″) is in the molecule centered at (010).

ment of all non-hydrogen atoms to convergence gave discrepancy indices of $R_1 = \Sigma\,||F_o| - |F_c||/|F_o| = 0.099$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.135$

The function minimized during all least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where the weighting factor is $w = 4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ [12].

Anisotropic refinement led to convergence in two full-matrix least squares cycles, with final discrepancy factors of $R_1 = 0.051$ and $R_2 = 0.074$. No attempt was made to locate hydrogen atoms. A final Fourier difference map revealed no peaks greater than 0.5 electrons per Å³. The error in an observation of unit weight was 1.479. Observed and calculated structure factors are listed in Table I.

Results and Discussion

The positional and thermal parameters are listed in Table II. The molecular structure and atom numbering scheme are shown in Figure 1, while the pertinent bond lengths and angles are given in Table III. The presence of an inversion center at the chromium atom requires the CrO_4 unit to be rigorously planar. The dihedral angle between the planes defined by the two CrO_4 units in the cell is 87.7°.

As often occurs in acetylacetonato complexes [6, 13], the C_3O_2 ligand skeleton is essentially planar but the metal atom is displaced slightly from the plane. In this case, the displacement of the chromium atom from the least-squares mean plane defined by O(1), O(2), C(2) and C(4) is 0.155Å. The deviation of C(1) and C(5) from this plane is statistically insignificant,

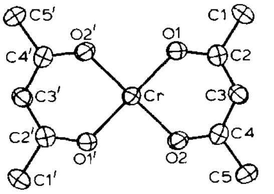

Figure 1. An Ortep drawing of the $Cr(C_5H_7O_2)_2$ molecule. Thermal ellipsoids enclose 50% of the electron density.

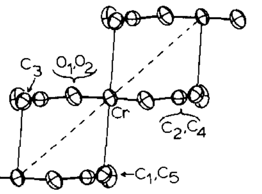

Figure 2. A simplified Ortep drawing of the stacking interactions in $Cr(C_5H_7O_2)_2$. The dotted lines represent the b axis.

but C(3) is out of the plane by a barely significant 0.034(5)Å. The existence of this distortion is evident in Figure 2, which shows the stacking of the molecules in the b direction. As the data in Table III indicate, the C(3) carbon atoms of the acetylacetonato ligands are located so as to occupy the axial positions with respect to the chromium atoms of adjacent molecules. The Cr–C distance, 3.048(5)Å, is much longer than the Cr–O distances, and the Cr–C(3)–C(2,4) angles average 95.4° and it is unlikely that there is much Cr–C σ bonding. This may be contrasted with the situation in $\{Pt(CH_3)_3[CH(OCC_3H_7)_2]\}_2$ where d(Pt–O) = 2.15Å *vs.* d(Pt–C) = 2.39Å, the Pt–C–C angles are 102°, and a genuine Pt–C σ bond is thought to exist [14]. The displacement of C(3) from the ligand plane is toward the chromium atom of the adjacent molecule, which may indicate that there is very weak bonding. One might also note that the contact distance between ligand planes is 3.048 + 0.155 + 0.034 = 3.24Å, rather less than the interplanar distance of 3.35Å in graphite [15] but greater than the very short 3.17Å stacking distance found for the radical anion of 7,7,8,8-tetracyanoquinodimethane in the TTF–TCNQ compound, where very strong intermolecular interactions have been demonstrated [16].

Comparison of the positional parameters in Table II with those published [17, 18] for $Cu(C_5H_7O_2)_2$ indicates that the compounds are isomorphous. The chromium compound thus becomes only the second example of a first row $M(C_5H_7O_2)_2$ complex known to be essentially a planar monomer, albeit with weak axial interactions in each case. Both $Cr(C_5H_7O_2)_2$ and $Cu(C_5H_7O_2)_2$ appear to be isomorphous [19] with $Pd(C_5H_7O_2)_2$ [20].

The other first-row transition metal $M(C_5H_7O_2)_2$ complexes whose structures have been determined are polymeric with bridging oxygen atoms giving higher coordination numbers to the metals. Thus the nickel and zinc compounds are trimers [5, 6] (with quite different geometries), while the cobalt compound is a tetramer [4]. For the other first row metals, the structures remain uncertain.

The chemistry of the vanadium compound seems to be restricted to complexes such as $V(C_5H_7O_2)_2(C_5H_5N)_2$ [21]. On the basis of spectroscopic data it has been suggested that $Ti(C_5H_7O_2)_2$ "may" adopt the trimeric structure of the nickel complex [22], and a similar assumption has been made from molecular weight measurements on $Mn(C_5H_7O_2)_2$ in hydrocarbon solvents [19, 23], X-ray powder diffraction studies have, however, shown that $Mn(C_5H_7O_2)_2$ is not isomorphous with the Zn, Ni, Co or Cu compounds. For $[Fe(C_5H_7O_2)_2]_x$ in benzene, x varies from 1 to 6 as a function of concentration [24]. Since, however, spectroscopic and molecular weight data on $Co(C_5H_7O_2)_2$ in solution [25] were not very suggestive of the tetrameric solid state structure which was ultimately demonstrated [4], not only the structures of the Ti, Mn and Fe complexes, but even their degrees of oligomerization must be regarded as unknown. One thus has a situation in which the literature on three $M(C_5H_7O_2)_2$ complexes, which are among the simplest examples of a widely studied and important class of compounds, that have been the subjects of at least three reviews [2, 3, 26], is devoid of some basic structural information.

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