in the octahedra can be determined by reference to a diagram of uranyl bond length *vs.* fractional valence given by Zachariasen (1954). The line relating these two quantities appears to have a slight curvature, and thus the equation of this line might reasonably be a quadratic. In a least-squares fit of a quadratic to the data, the coefficient of the X^2 term of the quadratic is small and does not deviate significantly from zero. This indicates that a straight line may fit the data as well as or better than a quadratic. In fact, a lower variance is obtained with a least-squares fit of a straight line to the data than with a quadratic and, therefore, the linear function is to be preferred for the representation of the data.

From the coefficients of the linear fit it is possible, by straightforward statistical techniques, to relate a bond length with a standard deviation to a fractional valence with a standard deviation. In Table 4 are given the interatomic distances and the associated fractional valences.

Table 4. *Interatomic distances and associated fractional valences in* $UO_2(OH)_2$

Atoms	Interatomic distances	Fractional valences
U-2 O(1)	$1{\cdot}82 \pm 0{\cdot}05$ Å	$1{\cdot}50 \pm 0{\cdot}18$
-2 O(2)	$2{\cdot}24 \pm 0{\cdot}06$	$0{\cdot}71 \pm 0{\cdot}16$
-2 O(2)	$2{\cdot}43 \pm 0{\cdot}06$	$0{\cdot}35 \pm 0{\cdot}14$

The sum of the fractional valences for the six bonds is $5{\cdot}12 \pm 0{\cdot}39$. The question now arises as whether the number 5·12 is significantly different from the normal valence of 6·00. By utilizing the statistical t test at the 95% confidence level, $t = 2{\cdot}45$ for a population of 6. Then, $2{\cdot}45 \times 0{\cdot}39 = 0{\cdot}96$, and $5{\cdot}12 + 0{\cdot}96 = 6{\cdot}08$. Thus at the 95% confidence level there is no significant difference between the empirically derived valence and the normal valence.

It has come to our attention that Zachariasen (1963) has devised an improved expression for the effects of secondary extinction. The ratio Zachariasen's formula/Dawson's formula is 1·00 for $2\theta = 0°$, 1·02 for $2\theta = 30°$ and 1·11 for $2\theta = 45°$. For Mo $K\alpha$ intensity data, where strong reflections occur only at low values of 2θ, it can be seen that no significant difference should occur in the structural parameters regardless of which formula is used. Zachariasen's formula applied to the data of the present paper resulted in no effective change in the parameters. This indicated that it would not be worthwhile to re-examine the Mo data of UF_4 and $UMoC_2$ in the light of Zachariasen's new formula.

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The Crystal Structure and Molecular Configuration of Trisacetylacetonatomanganese(III)*

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The crystal structure and molecular configuration of trisacetylacetonatomanganese(III) has been determined by X-ray diffraction techniques. The structure consists of discrete molecules linked together by van der Waals forces. The distortion of the octahedral configuration of oxygen ligands about the manganese atom appears to be the result of altered oxygen–metal–oxygen bond angles rather than of a Jahn–Teller mechanism.

Introduction

The departure from regular octahedral configuration for the case of nine 3*d* electrons, *i.e.* copper(II) compounds, is well documented (Griffith & Orgel, 1957). However, probably because of chemical instability, only a few examples of structure determinations for the transition elements with four unpaired electrons are available. These consist of simple halide compounds of Cr^{II} (Tracy, Gregory, Lingafelter, Dunitz,

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Mez, Rundle, Scheringer, Yakel & Wilkinson, 1961; Tracy, Gregory, Stewart & Lingafelter, 1962; Jack & Maitland, 1957) and MnF_3 (Hepworth & Jack, 1957). In addition to fluoride ions, the trivalent state of manganese can be stabilized by organic chelating groups. Trisacetylacetonatomanganese(III), $Mn(C_5H_7O_2)_3$, is an example of such a bidentate molecular complex.

Early crystal studies (Astbury, 1926) indicated the Mn complex to be isomorphous with several other trivalent metal acetylacetonates, including that of chromium(III). Recently, the crystal structure determination of the chromium complex appeared (Shkolnikova & Shugam, 1960). Together with Roof's (1956) results on the iron(III) complex, Forman & Orgel (1959) found their infrared data for the Cr, Mn and Fe complexes consistent with a Jahn–Teller distortion for the manganese complex. Unfortunately, their results do not in any way indicate the nature or extent of the distortion from octahedral symmetry, and it therefore seemed desirable to obtain structural evidence to clarify the extent of the Jahn–Teller mechanism in trisacetylacetonatomanganese(III).

Experimental

Crystals of trisacetylacetonatomanganese(III) were grown by slow evaporation at room temperature from an acetone solution. The complex was synthesized by allowing an acetylacetonate solution to react with freshly prepared manganese(III) hydroxide (Mellor, 1937).

Equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The following cell dimensions were obtained from rotation and zero-level Weissenberg photographs, a camera cassette standardized with NaCl ($a_0 = 5{\cdot}6387$ Å) being employed, and they are compared with values determined by Astbury (1926):

		Astbury
a_0	$= 13{\cdot}87_5 \pm 0{\cdot}015$	$14{\cdot}1$
b_0	$= 7{\cdot}467 \pm 0{\cdot}007$	$7{\cdot}68$
c_0	$= 16{\cdot}20_3 \pm 0{\cdot}025$	$16{\cdot}5$
β	$= 98{\cdot}42_7 \pm 0{\cdot}020$	$99{\cdot}4°$

Systematic absences of $0k0$ for $k = 2n+1$ and of $h0l$ for $l = 2n+1$ were consistent with the space group $P2_1/c$. With four molecules per unit cell, the calculated and observed densities were 1·406 and 1·427 respectively.

Two sets of partial three-dimensional intensity data were collected.

The first set of data was obtained by visually estimating unintegrated equi-inclination Weissenberg photographs and consisted of $h0l$ through $h4l$ and $hk0$ through $hk2$ nets taken with Cu $K\alpha$ radiation. No absorption correction was applied to the crystal specimen of nearly rectangular cross section ($0{\cdot}17 \times 0{\cdot}24$ mm) just under the 'ideal' optimum cross-sectional diameter of 0·29 mm (Buerger, 1942).

The second set of data was collected by means of a General Electric XRD 5 diffractometer with molybdenum radiation and yttrium and zirconium balanced filters. The 2θ scan technique with a 100-second pre-set counting time was used to determine 1047 unique reflections, of which 249 were considered to be unobserved. Absorption corrections were eventually calculated for the plate-like crystal specimen ($\mu = 9{\cdot}22$ cm^{-1}; $0{\cdot}2 \times 0{\cdot}5 \times 0{\cdot}5$ mm).

Lorentz and polarization factors were applied and structure factors calculated using Mn (Thomas & Umeda, 1957), C, O, and H (Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal, 1955) scattering factors and Mn dispersion corrections (Dauben & Templeton, 1955). Four reflections, 200, 020, 110, 002, were found to be considerably affected by secondary extinction and were omitted from all difference and differential syntheses and in calculation of R. Calculations were carried out on a CDC 1604 computer.

Determination of structure

A Patterson synthesis on $h0l$ of the first set of data was obtained with Beevers–Lipson strips and yielded $x = 0{\cdot}237$ and $z = -0{\cdot}037$ as the probable coordinates for the heavy atom. In order to contain the whole molecule within one quadrant, the coordinates for manganese were translated $\frac{1}{4}$ along c_0 (which is allowed for the $h0l$ projection of $P2_1/c$). The resulting heavy-atom Fourier synthesis revealed the probable orientation of the three acetylacetonate rings; however, calculations were set aside rather than proceed with the laborious strip technique.

With the availability of the necessary computer codes, a three-dimensional Patterson synthesis was calculated. Unfortunately, since the heavy atom lies close to $\frac{1}{4}\frac{1}{4}0$, atomic positions were obtained for the molecule which corresponded to that of the translated manganese of the $h0l$ projection. The resulting three-dimensional Fourier synthesis of course had the general molecular configuration which was expected since it was introduced by the calculated structure factors; however, refinement by the differential synthesis technique (Booth, 1946), corrected for series termination, resulted in high and unreasonable temperature factors. (R at this stage was approximately 0·30.) The eye estimation of the intensity data, rather than the interpretation of the Patterson synthesis, was the first item which came under suspicion. This became quite apparent after the second set of data was collected and the resulting three-dimensional Patterson synthesis was found to be very similar to that calculated with the eye estimated data. The balanced filter data were intuitively considered to be superior to those collected from the films and were, therefore, used in all remaining calculations.

A three-dimensional Fourier synthesis with the correct positional parameter coordinates for the manganese and oxygen clearly showed the parameter positions of all the carbon atoms. Before the observed intensities were corrected for absorption, these parameter positions, together with individual temperature factors, were refined by several differential syntheses. The resulting discrepancy factor, omitting unobserved reflections as well as the four reflections strongly affected by secondary extinction, was 0·09 (with no omitted reflections, $R=0·16$). At this point in the refinement, the intramolecular bond distances for the acetylacetonate ligands were considered inconsistent with chemical knowledge (for example, C–C single bonds varied from 1·47–1·54 Å). A three-dimensional difference synthesis was calculated. Assuming a C–H bond distance of 1·085 Å and orienting methyl groups to give the best overlap between hydrogen atoms and areas of high electron density, positional parameters for the hydrogen atoms (Table 1) were calculated and included as fixed atom contributions ($B=7·0$) in all subsequent refinement cycles.

Only a slight improvement on the interatomic bond distances was obtained. Therefore, in order to remove any possibilities of systematic errors, intensities were corrected for absorption, and dispersion corrections for manganese were introduced (Templeton, 1955).

Table 1. *Hydrogen atomic coordinates* ($B=7·0$)

	x	y	z
H(12)	−0·04715	0·21425	0·51776
H(36)	0·47320	0·54311	0·61472
H(45)	0·28590	0·03100	0·24136
H(X11)	−0·11113	0·35709	0·38891
H(X12)	−0·04039	0·30018	0·31201
H(X13)	−0·03333	0·51627	0·35498
H(X21)	0·00090	0·11790	0·65694
H(X22)	0·10748	−0·00789	0·66537
H(X23)	0·11090	0·21452	0·70055
H(X31)	0·57880	0·28823	0·62223
H(X32)	0·55278	0·14970	0·53519
H(X33)	0·51121	0·09360	0·62907
H(X41)	0·35806	0·28436	0·19311
H(X42)	0·30931	0·47756	0·23060
H(X43)	0·42485	0·40120	0·27544
H(X51)	0·22279	−0·24501	0·27516
H(X52)	0·13299	−0·22113	0·33940
H(X53)	0·25136	−0·28629	0·38222
H(X61)	0·38602	0·80194	0·62528
H(X62)	0·30329	0·83706	0·53483
H(X63)	0·26300	0·75696	0·62568

Table 2. *Final atom coordinates and isotropic temperature factors*

	x	y	z	B
Mn	0·24181	0·27001	0·46873	4·083
O(1)	0·12346	0·34002	0·40811	5·994
O(2)	0·19461	0·19383	0·56447	5·943
O(3)	0·36597	0·18904	0·51898	5·417
O(4)	0·30228	0·35685	0·38036	5·749
O(5)	0·21893	0·03713	0·42711	5·646
O(6)	0·25156	0·50025	0·51410	5·633
C(1)	0·04243	0·31655	0·43218	6·022
C(X1)	−0·04336	0·37463	0·36829	8·439
C(12)	0·02627	0·23990	0·50747	7·768
C(2)	0·10200	0·18631	0·56896	5·544
C(X2)	0·07883	0·12117	0·65398	7·865
C(3)	0·43052	0·29192	0·55901	5·182
C(X3)	0·52542	0·20095	0·58875	7·044
C(36)	0·41500	0·47009	0·57968	6·333
C(6)	0·32913	0·55984	0·55800	4·616
C(X6)	0·32080	0·75550	0·58874	8·521
C(X5)	0·20850	−0·20568	0·33581	7·565
C(4)	0·30846	0·26333	0·31259	5·485
C(X4)	0·35364	0·36056	0·24766	6·737
C(45)	0·27600	0·08934	0·30067	6·142
C(5)	0·23534	−0·01304	0·35373	4·700

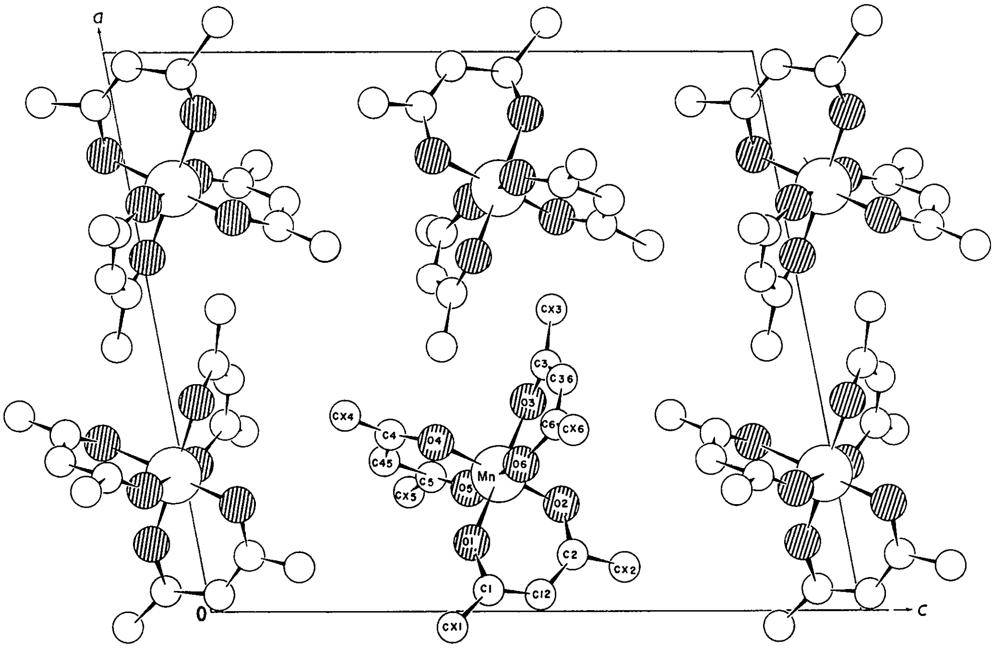

Fig. 1. Molecular arrangement viewed along the b_0 axis.

Table 3. *Observed and calculated structure factors*

H	10FO	10FC
K= 0 L= 0		
1	<120	160
2	1457	-1771
3	494	584
4	897	1054
5	50	32
6	634	-738
7	343	-400
8	289	340
9	322	412
10	242	-251
11	245	-276
K= 1 L= 0		
1	1698	-1935
2	166	-160
3	278	232
4	248	-217
5	417	-451
6	226	-194
7	489	563
8	<97	93
9	251	-268
10	194	-191
11	152	152
K= 2 L= 0		
0	1242	-1575
1	165	-181
2	204	205
3	96	-62
4	262	-194
5	<86	-32
6	107	69
7	158	161
8	137	-172
9	137	-149
10	149	146
K= 3 L= 0		
1	359	420
2	89	73
3	300	-300
4	93	-19
5	375	372
6	235	239
7	218	-220
8	<105	-90
9	280	297
10	187	190
K= 4 L= 0		
0	634	691
1	134	-123
2	602	-651
3	148	-148
4	596	650
5	313	314
6	395	-407
7	153	-134
8	247	259
K= 5 L= 0		
1	140	-155
2	<103	-44
3	315	339
4	244	215
5	375	-418
6	161	-151
7	244	205
K= 6 L= 0		
0	<114	-35
1	<114	36
2	160	159
3	<116	-58
K= 1 L= 1		
0	352	335
1	360	-350
2	122	113
3	703	789
4	243	261
5	521	-568
6	223	-207
7	318	348
8	<98	-17
9	105	-69
10	163	-156
11	<116	-78
K= 2 L= 1		
0	871	948
1	230	240
2	164	170
3	239	246
4	<83	-63
5	360	-385
6	387	416
7	<96	-80
8	140	-146
9	<107	-9
10	129	-113
K= 3 L= 1		
0	<93	6
1	733	-814
2	175	171
3	<87	61
4	364	-398
5	108	85
6	177	152
7	<102	-14
8	<107	25
9	125	-104
10	<118	39
K= 4 L= 1		
0	406	-427
1	260	234
2	198	191
3	226	-218
4	<99	-25
5	306	324
6	111	-57
7	<109	1
8	<114	-78
K= 5 L= 1		
0	118	104
1	<106	45
2	134	-117
3	<107	-15
4	329	335
5	<112	-17
6	312	-307
K= 6 L= 1		
0	<126	19
1	<119	-85
2	<117	-75
3	<118	41
K= 1 L= -1		
1	64	35
2	73	-9
3	81	36
4	231	-254
5	158	160
6	<86	15
7	291	293
8	<96	51
9	<101	18
10	<108	-70
11	138	-120
K= 2 L= -1		
1	280	-314
2	<74	-14
3	<77	-27
4	262	270
5	102	-81
6	197	199
7	<95	241
8	100	-87
9	154	-151
10	146	-120
11	<117	66
K= 3 L= -1		
1	249	268
2	130	129
3	<86	-27
4	127	-124
5	<92	24
6	173	176
7	206	-212
8	<105	-107
9	122	-92
10	165	160
K= 4 L= -1		
1	348	404
2	157	-137
3	316	-332
4	139	89
5	291	310
6	159	-114
7	113	-67
8	<112	-28
9	148	129
K= 5 L= -1		
1	<103	-30
2	158	-170
3	<105	37
4	161	154
5	<110	19
6	269	-262
7	145	106
K= 6 L= -1		
1	<115	-104
2	<115	67
3	153	143
K= 0 L= 2		
0	1849	2178
1	821	791
2	321	-361
3	1246	-1438
4	443	485
5	751	859
6	685	-766
7	401	-465
8	284	342
9	455	511
10	183	-177
11	<117	-115
K= 1 L= 2		
0	448	413
1	808	-806
2	1084	-1215
3	1032	1115
4	608	712
5	902	-1057
6	507	-527
7	562	666
8	232	241
9	306	-312
10	312	-323
11	<118	-51
K= 2 L= 2		
0	874	-927
1	325	-308
2	212	185
3	<82	0
4	392	-469
5	344	-327
6	393	435
7	185	172
8	328	-350
9	215	-209
10	181	173
K= 3 L= 2		
0	99	119
1	704	716
2	136	106
3	493	-494
4	115	-107
5	426	438
6	342	369
7	252	-265
8	201	-210
9	240	254
K= 4 L= 2		
0	663	698
1	111	97
2	250	-229
3	193	-170
4	318	369
5	383	416
6	150	-131
7	210	-223
8	130	117
K= 5 L= 2		
0	142	79
1	244	-264
2	247	-239
3	265	255
4	290	273
5	277	-266
6	192	-190
K= 6 L= 2		
0	<127	-57
1	<123	-37
2	123	124
3	<120	74
K= 0 L= -2		
1	618	-601
2	784	-799
3	991	1107
4	910	950
5	<79	70
6	362	-423
7	<90	-43
8	524	569
9	<100	1
10	431	-461
11	257	-255
K= 1 L= -2		
1	1206	-1261
2	126	79
3	390	-463
4	217	239
5	224	-275
6	463	-551
7	269	298
8	<96	20
9	359	-392
10	<107	-64
11	347	370
K= 2 L= -2		
1	90	-72
2	112	37
3	<79	43
4	295	-266
5	<86	9
6	148	172
7	103	84
8	263	-260
9	<105	47
10	279	277
11	<117	-2
K= 3 L= -2		
2	95	-78
3	252	-236
4	<89	51
5	347	399
6	<96	51
7	304	-313
8	<105	18
9	302	301
10	<116	-2
K= 4 L= -2		
1	158	-128
2	607	-612
3	239	227
4	537	540
5	121	-81
6	571	-594
7	<108	-7
8	401	413
9	<117	-28
K= 5 L= -2		
1	205	-201
2	158	159
3	239	255
4	<108	34
5	338	-338
6	174	-115
7	342	339
K= 6 L= -2		
1	<120	24
2	132	106
3	<117	-64
K= 1 L= 3		
0	471	504
1	173	-181
2	88	-57
3	124	-94
4	577	630
5	189	-170
6	499	-541
7	<97	-71
8	253	261
9	<108	31
10	197	-199
K= 2 L= 3		
0	765	840
1	472	519
2	295	-315
3	<85	-94
4	<88	-6
5	637	-693
6	<96	21
7	129	119
8	<105	-35
9	134	-73
10	<117	31
K= 3 L= 3		
0	281	288
1	751	-815
2	399	-430
3	372	394
4	114	-116
5	171	-180
6	<101	22
7	185	186
8	111	62
9	<116	-24
K= 4 L= 3		
0	438	-487
1	201	-195
2	154	156
3	<101	81
4	135	-142
5	160	140
6	114	124
7	<113	11
8	118	-130
K= 5 L= 3		
0	187	187
1	172	158
2	<112	-94
3	153	-147
4	338	342
5	<116	66
6	133	-94
K= 6 L= 3		
0	<128	96
1	<127	-35
2	<124	-77
K= 1 L= -3		
1	243	239
2	861	-975
3	87	-84
4	99	99
5	95	94
6	113	-102
7	<92	7
8	<97	30
9	<102	58
10	<108	-4
11	136	-96
K= 2 L= -3		
1	312	-345
2	148	-165
3	<81	-29
4	195	-185
5	<87	-43
6	<91	-32
7	<95	82
8	128	-102
9	<105	-68
10	111	-26
11	144	142
K= 3 L= -3		
1	630	655
2	170	187
3	<89	43
4	119	-82
5	<93	16
6	167	168
7	150	-134
8	<105	-27
9	<110	-62
10	146	147
K= 4 L= -3		
1	195	219
2	108	-55
3	371	-402
4	102	45
5	300	325
6	144	-111
7	231	-227
8	119	67
K= 5 L= -3		
1	122	-112
2	347	-379
3	110	-73
4	256	239
5	147	116
6	<327	-341
7	<117	12
K= 6 L= -3		
1	<125	-77
2	<120	95
3	142	151
K= 0 L= 4		
0	93	3
1	587	-627
2	129	146
3	108	113
4	317	328
5	845	907
6	144	-115
7	415	-503
8	309	313
9	429	461
10	225	-254
K= 1 L= 4		
0	339	298
1	312	-276
2	290	-274
3	349	381
4	491	500
5	356	-349
6	681	-706
7	<99	34
8	440	457
9	225	-223
10	282	-303
K= 2 L= 4		
0	390	-399
1	215	-213
2	224	218
3	207	196
4	347	-342
5	745	-779
6	288	289
7	447	526
8	273	-267
9	436	-453
K= 3 L= 4		
0	146	-63
1	485	488
2	305	306
3	273	-276
4	377	-349
5	183	184
6	353	374
7	174	-174
8	323	-337
9	163	149
K= 4 L= 4		
0	406	444
1	273	308
2	161	-151
3	283	-285
4	194	203
5	187	169
6	130	-121
7	157	-168
K= 5 L= 4		
0	138	205
1	294	-277
2	378	-377
3	196	172
4	197	172
5	<119	-94
K= 6 L= 4		
0	164	-167
1	173	-161
K= 0 L= -4		
1	<84	55
2	1264	-1474
3	526	551
4	376	367
5	129	-140
6	454	-515
7	173	165
8	660	675
9	445	-466
10	449	-478
11	177	181
K= 1 L= -4		
1	1146	-1253
2	922	991
3	268	272
4	296	-278
5	414	-443
6	150	-165
7	377	428
8	192	-182
9	559	-612
10	209	211
11	372	411
K= 2 L= -4		
1	<87	23
2	110	99
3	294	-322
4	213	-214
5	109	100
6	244	254
7	183	-164
8	253	-238
9	281	301
10	246	259
K= 3 L= -4		
1	598	592
2	365	-365
3	279	-312
4	343	330
5	378	384
6	236	-262
7	192	-190
8	185	173
9	146	123
10	<117	-76
K= 4 L= -4		
1	119	122
2	325	-301
3	357	388
4	416	436
5	267	-275
6	380	-360
7	224	220
8	274	244
K= 5 L= -4		
1	314	-271
2	260	230
3	281	267
4	266	-253
5	296	-294
6	166	173
K= 6 L= -4		
1	<128	29
2	181	159
K= 1 L= 5		
0	184	-200
1	<87	10
2	91	-60
3	215	-266
4	286	297
5	142	143
6	<99	34
7	192	-203
8	112	76
9	200	195
K= 2 L= 5		
0	213	179
1	105	79
2	300	-336
3	175	195
4	<95	52
5	108	-77
6	133	-122
7	123	-101
8	242	234
9	117	69
K= 3 L= 5		
0	342	327
1	336	-344
2	265	-271
3	219	238
4	<102	-18
5	108	-70
6	240	-227
7	<112	106
8	141	133
K= 4 L= 5		
0	357	-380
1	110	-80
2	195	211
3	117	-95
4	186	-183
5	<112	14
6	156	157
7	<119	47
K= 5 L= 5		
0	206	200
1	281	283
2	153	-93
3	212	-219
4	241	235
5	<122	28
K= 1 L= -5		
1	140	86
2	394	-473
3	317	-318
4	330	393
5	218	187
6	286	-316
7	160	-173
8	136	118
9	140	-90
10	<110	-41
11	<116	-13
K= 2 L= -5		
1	270	262
2	90	-53
3	170	167
4	321	349
5	173	-188
6	334	-330
7	141	145
8	<102	-54
9	<108	-28
10	<113	49
K= 3 L= -5		
1	597	620
2	<96	-6
3	95	64
4	134	-112
5	<97	-20
6	259	291
7	110	-69
8	<108	-54
9	141	113
K= 4 L= -5		
1	201	180
2	123	-94
3	326	-349
4	111	76
5	281	278
6	185	-171
7	251	-275
8	228	200
K= 5 L= -5		
1	265	-257
2	353	-366
3	155	120
4	249	239
5	177	-154
6	232	-239
K= 0 L= 6		
0	203	-182
1	444	401
2	109	-52
3	209	-242
4	568	526
5	645	707
6	<101	-81
7	322	-355
8	212	211
9	190	173
K= 1 L= 6		
0	214	206
1	<93	6
2	162	-129
3	187	192
4	374	401
5	<99	-118
6	340	-365
7	120	-84
8	314	312
9	<117	-64
K= 2 L= 6		
0	134	-92
1	431	-427
2	184	184
3	467	471
4	185	-154
5	608	-634
6	<106	-29
7	382	365
8	<115	54
K= 3 L= 6		
0	251	-241
1	219	213
2	180	162
3	129	-136
4	328	-341
5	<108	79
6	274	287
7	<116	-16
8	220	-229
K= 4 L= 6		
0	239	238
1	401	385
2	247	-253
3	296	-291
4	174	137
5	117	113
6	<119	-79
K= 5 L= 6		
0	413	403
1	175	-163
2	364	-347
3	<123	71
4	<124	76
K= 0 L= -6		
1	115	127
2	636	-704
3	774	845
4	510	548
5	551	-577
6	492	-566
7	232	236
8	324	338
9	393	-434
10	290	-296
11	210	230
K= 1 L= -6		
1	111	-73
2	965	1068
3	351	367
4	943	-1023
5	220	-186
6	432	474
7	175	184
8	300	-307
9	305	-303
10	300	327
K= 2 L= -6		
1	534	551
2	199	171
3	780	-872
4	<93	-8
5	206	193
6	150	137
7	217	-245
8	177	-172
9	241	242
10	208	193
K= 3 L= -6		
1	356	353
2	510	-501
3	243	-222
4	418	423
5	181	157
6	203	-217
7	146	-143
8	213	181
9	239	223
K= 4 L= -6		
1	246	-223
2	218	-206
3	360	391
4	167	148
5	136	-124
6	122	-78
7	143	135
8	300	289
K= 5 L= -6		
1	192	-154
2	369	343
3	<117	10
4	369	-356
5	<118	28
K= 1 L= 7		
0	101	62
1	107	-98
2	208	-189
3	<99	32
4	176	163
5	<103	54
6	112	85
7	<111	-35
8	<116	8
K= 2 L= 7		
0	<102	-27
1	178	-157
2	112	-86
3	332	341
4	165	137
5	235	220
6	<110	-67
7	137	-127
8	130	111
K= 3 L= 7		
0	<108	27
1	<109	-57
2	<108	43
3	219	224
4	<110	-2
5	147	-128
6	167	-151
7	<120	85
K= 4 L= 7		
0	176	-173
1	125	-88
2	317	324
3	<117	-42
4	242	-228
5	<120	-118
K= 5 L= 7		
0	<126	7
1	242	229
2	173	-131
3	232	-229
K= 1 L= -7		
1	276	313
2	417	-419
3	232	-245
4	427	464
5	112	-88
6	156	-178
7	<119	-13
8	<104	54
9	<109	-44
10	<114	51
K= 2 L= -7		
1	236	-236
2	145	114
3	476	505
4	<97	-46
5	160	-180
6	161	158
7	148	178
8	<108	33
9	<112	60
10	<117	49
K= 3 L= -7		
1	194	194
2	<105	48
3	165	-143
4	<103	-39
5	277	261
6	112	113
7	154	-134
8	<113	-9
9	117	140
K= 4 L= -7		
1	<115	-16
2	133	-109
3	<111	-46
4	127	102
5	128	111
6	162	-145
7	170	-165
K= 5 L= -7		
1	157	-152
2	<123	-15
3	<121	34
4	<121	30
K= 0 L= 8		
0	243	-238
1	320	304
2	<102	62
3	313	-326
4	176	-169
5	307	301
6	178	178
7	285	-272
8	<120	58
K= 1 L= 8		
0	172	148
1	<103	39
2	146	-140
3	139	-123
4	402	404
5	234	250
6	337	-340
7	<116	-110
8	258	258
K= 2 L= 8		
0	159	140
1	474	-457
2	174	-172
3	466	456
4	132	103
5	402	-392
6	182	-162
7	258	263
K= 3 L= 8		
0	397	-389
1	153	-134
2	446	450
3	128	115
4	434	-428
5	118	74
6	376	371
K= 4 L= 8		
0	149	-124
1	450	452
2	<121	61
3	303	-276
4	<123	64
K= 5 L= 8		
0	253	248
1	151	100
K= 0 L= -8		
1	328	-343
2	144	99
3	943	1012
4	297	335
5	441	-480
6	160	-167
7	262	316
8	372	387
9	238	-259
10	355	-355
K= 1 L= -8		
1	194	223
2	616	653
3	262	270
4	727	-791
5	<99	91
6	348	384
7	116	101
8	239	-248
9	237	-207
10	251	272
K= 2 L= -8		
1	614	596
2	104	75
3	782	-822
4	<101	50
5	330	337
6	<104	45
7	254	-272
8	219	-213
9	187	182
K= 3 L= -8		
1	<111	-20
2	412	-286
3	219	-199
4	335	357
5	158	138
6	272	-266
7	212	-183
8	305	313
K= 4 L= -8		
1	329	-307
2	<118	-43
3	191	177
4	<115	88
5	204	-201
6	142	-112
K= 5 L= -8		
1	<128	77
2	<127	84
3	<125	-28
K= 1 L= 9		
0	203	198
1	233	241
2	342	-352
3	132	-120
4	<111	78
5	<114	-14
6	<117	-59
7	<121	-20
K= 2 L= 9		
0	255	252
1	228	-216
2	244	-236
3	211	194
4	<114	52
5	186	148
6	<120	-5
K= 3 L= 9		
0	<132	-16
1	253	-248
2	224	204
3	230	244
4	<120	83
5	<122	-30
K= 4 L= 9		
0	<124	12
1	<124	13
2	210	208
3	<127	-75
K= 1 L= -9		
1	<106	36
2	<104	53
3	161	-141
4	111	159
5	<103	24
6	161	-158
7	<108	-37
8	<111	66
9	<115	82
K= 2 L= -9		
1	<109	-6
2	145	131
3	216	-170
4	191	-215
5	<107	16
6	223	229
7	<111	50
8	<114	14
9	148	113
K= 3 L= -9		
1	120	92
2	211	-187
3	214	-206
4	189	163
5	212	230
6	115	-53
7	159	-152
K= 4 L= -9		
1	201	-125
2	<122	-29
3	141	105
4	<120	50
5	<120	17
K= 0 L= 10		
0	185	-169
1	295	247
2	116	106
3	228	-207
4	214	-191
5	<118	34
6	<122	76
K= 1 L= 10		
0	414	409
1	144	131
2	380	-364
3	292	-280
4	254	245
5	236	232
6	235	-219
K= 2 L= 10		
0	<115	62
1	399	-383
2	284	-268
3	322	317
4	259	239
5	204	-202
K= 3 L= 10		
0	290	-274
1	219	-201
2	355	347
3	317	302
4	237	-217
K= 4 L= 10		
0	<128	-61
1	139	143
K= 0 L= -10		
1	387	-375
2	191	186
3	414	412
4	<106	3
5	456	-485
6	262	264
7	456	494
8	126	98
9	119	-124
K= 1 L= -10		
1	123	83
2	397	398
3	213	188
4	554	-570
5	129	107
6	456	456
7	<112	-2
8	262	-274
K= 2 L= -10		
1	448	420
2	<113	3
3	655	-643
4	<111	7
5	514	510
6	190	-161
7	300	-308
8	<119	-79
K= 3 L= -10		
1	184	-168
2	310	-297
3	<118	-59
4	355	337
5	<118	-13
6	234	-213
K= 4 L= -10		
1	192	-157
2	127	102
3	213	207
4	<125	-13
K= 1 L= 11		
0	<117	2
1	146	113
2	<119	-100
3	148	-118
4	130	-91
5	<125	5
K= 2 L= 11		
0	<120	5
1	<121	-80
2	166	-126
3	140	-96
4	<126	32
K= 3 L= 11		
0	155	127
1	159	-135
2	<128	49
K= 1 L= -11		
1	<116	-67
2	143	98
3	<114	-6
4	<114	52
5	<114	30
6	139	-122
7	<117	18
K= 2 L= -11		
1	164	118
2	<119	-18
3	203	-154
4	117	-86
5	<117	32
6	<119	78
7	151	-97
K= 3 L= -11		
1	<124	-10
2	222	-189
3	139	-112
4	200	160
5	134	109
K= 0 L= 12		
0	<121	-22
1	341	306
2	311	264
3	189	-146
K= 1 L= 12		
0	357	337
1	282	251
2	393	-351
3	457	-403
K= 2 L= 12		
0	171	157
1	383	-346
2	341	-316
K= 0 L= -12		
1	285	-244
2	207	206
3	<119	34
4	279	-258
5	119	-94
6	328	318
K= 1 L= -12		
1	231	195
2	268	258
3	234	-211
4	329	-269
5	266	249
6	214	214
K= 2 L= -12		
1	347	303
2	174	-147
3	407	-365
4	<123	55
5	406	395
K= 1 L= 13		
0	<128	-91
1	<129	22
K= 1 L= -13		
1	151	-110
2	<126	133
3	<126	13
4	129	-99

The resulting refined structure ($R=0{\cdot}088$; shifts $<0{\cdot}1\ \sigma$) differed only by several hundredths of 1 Å in a few of the carbon atoms from that in which no corrections had been included. At all latter stages of the refinement, with or without corrections, the octahedral environment about the manganese remained distorted and the variation of the carbon–carbon single bond remained large.

The final values of the position and thermal parameters are given in Table 2 and observed and calculated structure factors in Table 3. The molecular arrangement is illustrated in Fig. 1. The average estimated standard deviation of the positional parameters calculated by the method of Cruickshank (1949) are 0·0017, 0·0075 and 0·012 Å for Mn, O and C respectively.

Discussion

From magnetic susceptibility studies (Jarrett, 1957), the electronic configurations of the acetylacetonates of Cr$^{\mathrm{III}}$, Mn$^{\mathrm{III}}$ and Fe$^{\mathrm{III}}$ are known to be of the high spin type (*i.e.* maximum number of allowed unpaired 3*d* electrons). Therefore it is predicted (Dunitz & Orgel, 1957) that the Mn$^{\mathrm{III}}$ complex, susceptible to a Jahn–Teller mechanism, might distort its immediate octahedral configuration to four shorter and two longer (or two shorter and four longer) metal–ligand bond lengths as is characteristic of Cu$^{\mathrm{II}}$, Cr$^{\mathrm{II}}$ and Mn$^{\mathrm{II}}$ compounds. However, it should be pointed out any other distortion which destroys the cubic symmetry of the immediate environment of the metal ion would also be acceptable (*e.g.* CuCl_4^{2-} and CuBr_4^{2-} ions, Morosin & Lingafelter, 1960). Using the numbering scheme illustrated in Fig. 2, Tables 4 and 5 list the bond lengths and bond angles respectively, determined with the indicated estimated standard deviations (e.s.d.). In Table 4, it may be noted that the averages of the deviations from the mean (m.d.) of the C–O and ring C–C bond lengths appear to be slightly larger than the e.s.d. (Cruickshank). This is consistent with the results of other investigations (Jacobsen, Wunderlich & Lipscromb, 1961; King, 1962; Smith, 1962).

Table 4. *Intramolecular bond lengths*

		Average	m.d.	e.s.d.
Mn–O(1)	1·861 Å			
Mn–O(2)	1·860			
Mn–O(3)	1·893			
Mn–O(4)	1·880			
Mn–O(5)	1·875			
Mn–O(6)	1·868			
		1·872	0·010	0·008
O(1)–C(1)	1·255			
O(2)–C(2)	1·299			
O(3)–C(3)	1·282			
O(4)–C(4)	1·315			
O(5)–C(5)	1·298			
O(6)–C(6)	1·280			
		1·288	0·015	0·014
C(1)–C(12)	1·395			
C(2)–C(12)	1·396			
C(3)–C(36)	1·396			
C(6)–C(36)	1·367			
C(4)–C(45)	1·379			
C(5)–C(45)	1·336			
		1·378	0·018	0·017
C(1)–C(*X*1)	1·522			
C(2)–C(*X*2)	1·539			
C(3)–C(*X*3)	1·497			
C(4)–C(*X*4)	1·490			
C(5)–C(*X*5)	1·503			
C(6)–C(*X*6)	1·553			
		1·517	0·021	0·017

Table 5. *Intramolecular bond angles*

O(1)–Mn–O(2)	97·75 ± 0·6°
O(3)–Mn–O(6)	96·65
O(4)–Mn–O(5)	96·72
Mn–O(1)–C(1)	123·93 ± 0·8
Mn–O(2)–C(2)	122·16
Mn–O(6)–C(6)	123·06
Mn–O(3)–C(3)	123·40
Mn–O(4)–C(4)	123·00
Mn–O(5)–C(5)	123·40
O(1)–C(1)–C(12)	126·52 ± 0·9
O(2)–C(2)–C(12)	126·50
O(3)–C(3)–C(36)	124·86
O(6)–C(6)–C(36)	127·06
O(5)–C(5)–C(45)	124·87
O(4)–C(4)–C(45)	123·87
C(1)–C(12)–C(2)	122·74 ± 0·9°
C(6)–C(36)–C(3)	124·37
C(5)–C(45)–C(4)	127·52
O(1)–C(1)–C(*X*1)	113·32 ± 0·9
O(2)–C(2)–C(*X*2)	113·71
O(3)–C(3)–C(*X*3)	114·04
O(4)–C(4)–C(*X*4)	114·62
O(5)–C(5)–C(*X*5)	112·41
O(6)–C(6)–C(*X*6)	114·15
C(12)–C(1)–C(*X*1)	120·12 ± 0·9
C(12)–C(2)–C(*X*2)	119·69
C(36)–C(3)–C(*X*3)	120·95
C(45)–C(4)–C(*X*4)	121·51
C(45)–C(5)–C(*X*5)	122·64
C(36)–C(6)–C(*X*6)	118·79

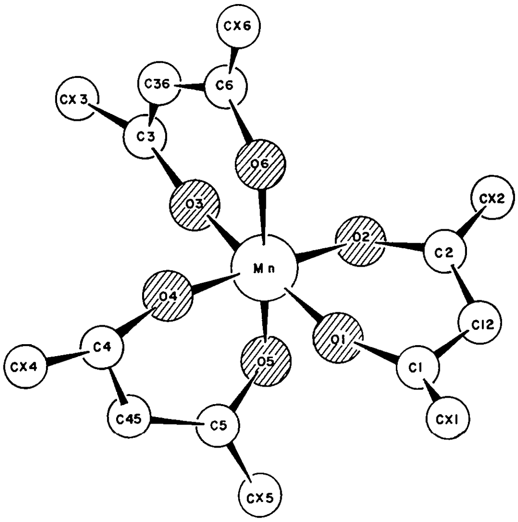

Fig. 2. Labeling scheme for trisacetylacetonatomanganese(III).

Table 6. *Intermolecular (nearest neighbor) distances and angles*

C(*X*1) 1·522		C(*X*2) 1·539		C(*X*3) 1·497	
5 C(12)	3·50(82)	6 C(*X*1)	3·74(105)	4 C(*X*5)	3·72(152)
6 C(*X*2)	3·74(82)	5 C(*X*1)	3·81(69)	4 C(45)	3·75(165)
5 C(*X*2)	3·81(115)	7 C(*X*4)	3·89(91)	7 C(*X*4)	3·78(70)
11 C(*X*2)	4·08(102)	7 C(45)	3·99(98)	4 C(*X*6)	3·84(106)
5 C(*X*6)	4·13(118)	7 C(*X*1)	4·08(158)	3 C(36)	3·85(76)
5 C(*X*1)	4·65(55)	9 C(*X*5)	4·47(134)	4 C(*X*3)	4·14(93)
1 C(*X*5)	4·78(76)	2 C(*X*6)	4·57(74)	2 C(*X*6)	4·37(79)
				3 C(*X*4)	4·39(96)

C(*X*4) 1·490		C(*X*5) 1·503		C(*X*6) 1·553	
11 C(*X*3)	3·78(143)	2 O(4)	3·55(140)	3 C(*X*3)	3·84(76)
10 C(*X*6)	3·84(145)	4 C(*X*3)	3·72(74)	8 C(*X*4)	3·84(156)
11 C(36)	3·86(110)	2O(1)	3·83(150)	5 C(*X*1)	4·13(89)
11 C(*X*2)	3·89(78)	2 C(*X*4)	4·17(134)	1 C(*X*5)	4·18(78)
1 C(*X*5)	4·17(82)	2 C(*X*6)	4·18(80)	1 C(*X*3)	4·37(130)
3 C(*X*3)	4·39(96)	12 C(*X*2)	4·47(149)	7 C(45)	4·41(74)
		11 C(*X*6)	4·52(98)	7 C(*X*5)	4·52(105)
		2 C(*X*1)	4·78(140)	1 C(*X*2)	4·57(137)

Intermolecular distances (in Å) for each methyl carbon atom are followed in parenthesis by the C(i)–C(Xi)–C(intermolecular) angle. The C(i)–C(Xi) intramolecular bond distances are shown after each methyl carbon atom. The numbers preceding the atoms involved in the intermolecular contacts refer to the following positions

1. $x, 1+y, z$
2. $x, -1+y, z$
3. $1-x, 1-y, 1-z$
4. $1-x, -y, 1-z$
5. $-x, 1-y, 1-z$
6. $-x, -y, 1-z$
7. $x, \frac{1}{2}-y, \frac{1}{2}+z$
8. $x, 1\frac{1}{2}-y, \frac{1}{2}+z$
9. $x, -\frac{1}{2}-y, \frac{1}{2}+z$
10. $x, 1\frac{1}{2}-y, -\frac{1}{2}+z$
11. $x, \frac{1}{2}-y, -\frac{1}{2}+z$
12. $x, -\frac{1}{2}-y, -\frac{1}{2}+z$

The somewhat higher discrepancy between m.d. and e.s.d. for the ring carbon–methyl carbon C(i)–C(Xi) may be explained by considering the nearest neighbor interactions. Table 6 lists these interactions together with the angle formed between the bond direction and the particular intermolecular (nearest neighbor) distance. It may be noted that the shorter C(i)–C(Xi) (i=3, 4, and 5) bond distances are those directed (angle greater than 120°) towards the closer nearest neighbors (less than 4·0 Å, which may be taken as twice the expected radius for a methyl radical). The interactions at right angles to C(X2), C(X3), and particularly C(X5) explain the very small departure from the chelate plane of these atoms.

In Fig. 3, the average values of the intramolecular bond lengths of three acetylacetonates are compared and found to be in acceptable agreement with each other and with the expected delocalization of π electrons resulting in partial double bond character in this type of chelate ring. The 1·875 Å Mn–O bond distance may be compared with the mean value of 1·95 ± 0·01 Å and 1·90 ± 0·03 Å, respectively, reported for the iron(III) and chromium(III)[*] complex. Forman & Orgel's infrared study, corroborated by other investigators (Nakamoto, McCarthy, Ruby & Martell, 1961; Lawson, 1961) suggested that the Mn^{III} ion, having only one electron in the two anti-bonding e_g orbitals, would distort its octahedral environment and attain both the weaker iron–oxygen-like bonds and the stronger chromium–oxygen-like bonds. The spectral studies did, in fact, indicate a close resemblance of the Mn^{III} infrared spectrum to the superposition of the spectra of the Cr^{III} and Fe^{III} complexes.

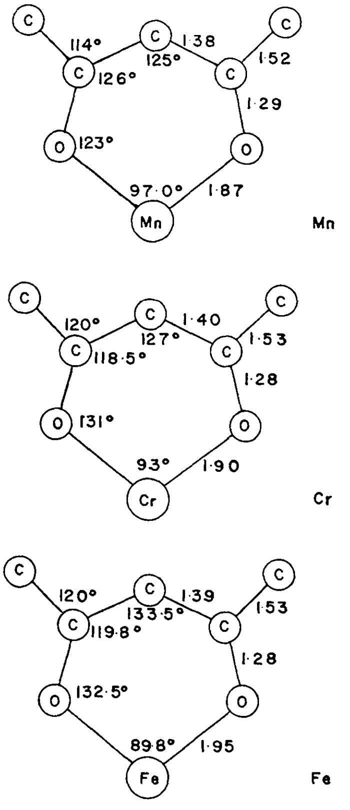

Fig. 3. Average intramolecular bond lengths for the chromium, iron and manganese complexes.

Table 7. *Oxygen–oxygen distances found in the distorted octahedron*

O(1)–O(2)	2·802	O(1)–O(5)	2·616
O(3)–O(6)	2·809	O(3)–O(4)	2·610
O(4)–O(5)	2·805	O(2)–O(6)	2·591
O(1)–O(4)	2·589	O(2)–O(3)	2·591
O(4)–O(6)	2·605	O(3)–O(5)	2·603
O(6)–O(1)	2·579	O(5)–O(2)	2·580

It appears that within the estimated standard deviations of this structure determination, the Mn–O bond distances are not significantly different.

A more detailed analysis of this structure does reveal an interesting distortion from octahedral symmetry of the oxygen surrounding the manganese atom. The oxygen–oxygen distances forming the edges

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[*] It should be pointed out, however, that investigators should be cautious in using the chromium(III) data in any quantitative manner since the reported R of 0·288 appears to be the result of an error in the structure determination. Together with several other transition metal acetylacetonates, this structure is currently being reinvestigated.

of the octahedron are listed in Table 7. Three of these distances are significantly different from the other nine. Fig. 4 shows a view of the distorted octahedron down the only remaining threefold axis after the removal of cubic symmetry. The amount of 'twist' of the upper triangle formed by O(2), O(3), and O(5) relative to the lower triangle (O(1), O(4), and O(6)) is approximately 7·5°.

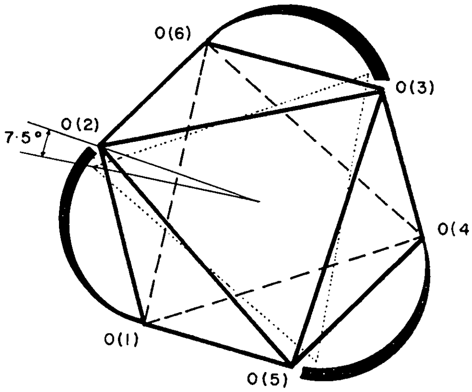

Fig. 4. Distorted octahedral environment in trisacetylacetonatomanganese(III) viewed down the remaining threefold axis. The upper face of the octahedron, formed by O(2), O(3), and O(5), is rotated approximately 7·5° from the position required for a perfect octahedron (small dash) as is found in the iron(III) complex.

This distortion, however, may not be the result of a Jahn–Teller mechanism. The shorter Mn–O bond distances compared with the Fe–O bond distances, where theoretically and experimentally an octahedral environment is found, suggests that it is energetically more favorable to retain the wider 'bite' (O–O distance equal to 2·80 Å) of the bidentate ring than to preserve cubic symmetry as the metal–oxygen distance is decreased. The average O–Mn–O bond angle of 96·9° is consistent with the 2·80 Å O–O separation and the 1·875 Å Mn–O bond distance. It is also interesting to note that this 2·80 Å O–O distance is retained even when the metal–oxygen distance is increased to 2·40 Å (Matković & Grdenić, 1963).

The distorted octahedral coordination found about the Mn atom appears to explain the infrared absorption spectra irrespective of whether a Jahn–Teller mechanism is operative. The behavior of the absorption bands between 200–900 cm^{-1} suggest that the transitions arise from a coupling of vibrational modes including that of metal–oxygen bending rather than a pure metal–oxygen vibration. Thus the two types of O–Mn–O bond angles (96·9° and 87·8°) compared with the single 90° O–Fe–O bond angle result in the appearance of two different bands in the Mn^{III} complex for each band found in the spectra of the Fe^{III} complex.

Note added in proof. — We have redetermined the crystal structure of the chromium(III) complex (R = 0·07). The molecular packing is essentially identical with that of the manganese(III) complex rather than that proposed by Shkolnikova & Shugam (1960). In addition, discrepancies between the interatomic bond distances and atomic coordinate positions listed in Roof's determination of the iron(III) complex have been found.

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