CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Crystal and Molecular Structure of Guaiazulenedimolybdenum Hexacarbonyl

BY MELVYN R. CHURCHILL AND PETER H. BIRD

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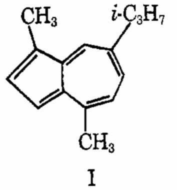
Guaiazulenedimolybdenum hexacarbonyl, $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$, crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}^5; no. 14) with unit-cell parameters $a = 11.82 \pm 0.02$ Å, $b = 16.39 \pm 0.02$ Å, $c = 10.95 \pm 0.02$ Å, $\beta = 99.31 \pm 0.10°$, $Z = 4$. Observed and calculated densities are, respectively, 1.75 ± 0.03 and 1.770 g cm^{-3}. A single-crystal X-ray structural analysis, based on complete three-dimensional data to $\sin\theta = 0.38$ (Mo Kα radiation) collected with a 0.01°-incrementing Buerger automated diffractometer, has been completed. Patterson, Fourier, and least-squares refinement techniques have led to the location of all atoms other than the methyl hydrogens. The final discrepancy index is $R_F = 7.57\%$ for 1766 independent nonzero reflections. The crystal consists of discrete molecular units of $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$ separated by normal van der Waals contacts. Two $Mo(CO)_3$ groups lie on the same side of the azulene ligand and are linked by a molybdenum–molybdenum bond of length 3.267 ± 0.006 Å. One molybdenum atom is bonded to the carbon atoms of the five-membered ring *via* a π-cyclopentadienyl→metal bond, while the other molybdenum atom bonds to the remaining five carbon atoms of the azulene skeleton *via* a π-pentadienyl→metal linkage.

Introduction

A number of azulene–metal–carbonyl complexes have been reported during the past 10 years.[1-8] While the stoichiometry of these complexes is usually well-established, there is often some ambiguity in their detailed molecular configuration. Thus, definitive information on the structures of $C_{10}H_8Fe_2(CO)_5$,[9,10] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[11,12] $C_{10}H_8Mn_2(CO)_6$,[6] $(CH_3)_3C_{10}H_5Ru_4(CO)_9$,[7] and $(C_{10}H_8)_2Fe_4(CO)_{10}$[8] has only recently been obtained *via* X-ray diffraction studies.

Preliminary crystallographic results on the *triclinic*[13] and *monoclinic*[14] modifications of $C_{10}H_8Mo_2(CO)_6$ have revealed that the molecule has the structure proposed by King and Bisnette[5] but, in each case, disorder within the crystal lattice has precluded an *accurate* determination of the molecular geometry. To continue our systematic investigations of azulene–metal–carbonyl complexes[6-13] and to obtain detailed information on the geometry of the $AzMo_2(CO)_6$ system (Az = azulene or substituted azulene), we have examined the crystal structure of guaiazulenedimolybdenum hexacarbonyl. [Guaiazulene is the trivial name for 7-isopropyl-1,4-dimethylazulene (I).] An account of this structure at an intermediate stage of refinement has already appeared.[13]



I

Collection and Reduction of X-Ray Data

Guaiazulenedimolybdenum hexacarbonyl was prepared by the method of Burton, *et al.*[3] Crystals of a size suitable for X-ray diffraction studies were grown by slow cooling of a saturated solution in cyclohexane–ethylene dichloride. The complex is air stable and is not X-ray sensitive.

Optical examination and the observed reciprocal lattice symmetry of C_{2h} (2/m) indicate that the crystals belong to the monoclinic system. Unit-cell parameters, obtained from calibrated ($a_{NaCl} = 5.640$ Å) $h0l$ and $hk0$ precession photographs taken with Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) at 23 ± 2°, are $a = 11.82 \pm 0.02$ Å, $b = 16.39 \pm 0.02$ Å, $c = 10.95 \pm 0.02$ Å, $\beta = 99.31 \pm 0.10°$. [The errors associated with the unit-cell constants are derived from the sum of the inaccuracies involved in measuring (from precession films) the positions of diffraction rows from the crystal under investigation and from the standard sodium chloride crystal. They are probably overestimates.] The unit-cell volume is 2094 Å^3. The observed density ($\rho_{obsd} = 1.75 \pm 0.03$ g cm^{-3}, by flotation in aqueous zinc iodide solution) is in satisfactory agreement with the value calculated for $Z = 4$ ($\rho_{calcd} = 1.770$ g cm^{-3} and $M = 558.3$ for $C_{21}H_{18}O_6Mo_2$). A survey of $hk0$, $hk1$, $hk2$, $h0l$, $h1l$, $h2l$ precession photographs and $0kl$, $1kl$, $2kl$ Weissenberg photographs revealed the systematic absences: $h0l$ for $h + l = 2n + 1$, $0k0$ for $k = 2n + 1$. The space group is therefore $P2_1/n$, a nonstandard setting of space group no. 14 (C_{2h}^5) having the equipoints: x, y, z; $-x, -y, -z$; $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$.

Diffraction data were collected from two crystals, each of which was a parallelepiped. Crystal I (0.30 × 0.10 × 0.10 mm) was mounted on its extended a axis; crystal II (0.14 × 0.12 × 0.12 mm) was mounted along its c axis. [Dimensions in each case refer sequentially to the a, b, c directions in the crystal.] Intensity data

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[1] R. Burton and G. Wilkinson, *Chem. Ind.* (London), 1205 (1958).
[2] R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *ibid.*, 1592 (1958).
[3] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).
[4] E. O. Fischer, Abstracts, Organometallic Chemical Symposium, Cincinnati, Ohio, June 1963, p 66.
[5] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).
[6] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 145 (1968).
[7] M. R. Churchill and P. H. Bird, *J. Am. Chem. Soc.*, **90**, 800 (1968).
[8] M. R. Churchill and P. H. Bird, *ibid.*, **90**, 3241 (1968).
[9] M. R. Churchill, *Chem. Commun.*, 450 (1966).
[10] M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).
[11] P.H. Bird and M. R. Churchill, *Chem. Commun.*, 705 (1967).
[12] P. H. Bird and M. R. Churchill, *Inorg. Chem.*, **7**, 349 (1968).
[13] M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).
[14] J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).

(Mo Kα radiation, $\bar{\lambda}$ 0.7107 Å) were collected with a 0.01°-incrementing Buerger automated diffractometer using the standard "stationary-background, ω-scan, stationary-background" counting sequence. The apparatus, experimental method, and precautions have been described at length in a previous paper.[12] Details specific to the present analysis follow. (i) The angle scanned (ω) is given by $\omega = [2.0 + (0.8/L)]°$, where $1/L$ is the Lorentz factor. (ii) The scan speed was 2°/min. (iii) Backgrounds (B_1 and B_2 counts) were measured for half the time of the main scan (C counts). (iv) Within a level, check reflections were remeasured after data had been collected for each batch of 20 reflections. No appreciable (*i.e.*, $\geqslant 3(\text{count})^{1/2}$) variations from the mean were detected, indicating stability both of sample and of electronics. (v) $I(hkl)$, the intensity of the reflection hkl, was calculated as

$$I(hkl) = C(hkl) - [B_1(hkl) + B_2(hkl)]$$

Data were assigned standard deviations according to the following scheme (where $\delta(hkl) = 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$—*i.e.*, the maximum probable error based solely on counting statistics): $I(hkl) > 625$, $\sigma(hkl) = 0.1[I(hkl)]$; $625 \geqslant I(hkl) \geqslant \delta(hkl)$, $\sigma(hkl) = 2.5[I(hkl)]^{1/2}$; $I(hkl) < \delta(hkl)$, reflection rejected.

Equiinclination geometry was used in collecting data for the zones $0kl$ through $12kl$ from crystal I. [This represents data complete to $\sin\theta = 0.38$, which includes over 95% of the data visible on long-exposure $0kl$, $1kl$, and $2kl$ Weissenberg photographs. While a few further data *could* have been collected, the ratio of observable data to unobservable data beyond $\sin\theta = 0.38$ is very low.] Levels $hk0$ through $hk5$ were collected from crystal II in order to correlate the a-axis data. The maximum counting rate was $\sim 5 \times 10^4$ counts/sec; since the dead time of the counter is appreciably less than 1 μsec, no corrections for coincidence losses were applied.

The linear absorption coefficient, $\mu = 12.2\ \text{cm}^{-1}$ for Mo Kα radiation, is sufficiently small and the crystals are sufficiently close to cylindrical and spherical (respectively) that no absorption corrections were applied. [The maximum variations in transmission coefficient are estimated at less than 5%.] Following correction for Lorentz and polarization effects [$\text{Lp}^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)$],[15,16] data were placed on a common scale using a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.[17] A Wilson plot based on the resulting 1766 independent reflections yielded an approximate absolute scale factor and the over-all isotropic thermal parameter, $B = 2.13$ Å^2.

Elucidation and Refinement of Structure

Coordinates for the two molybdenum atoms ($x_1 = 0.223$, $y_1 = 0.082$, $z_1 = -0.178$; $x_2 = 0.227$, $y_2 = 0.212$, $z_2 = 0.043$) were obtained from a three-dimensional Patterson synthesis[18] which had been sharpened such that the average intensity was independent of $\sin\theta$ and which had the origin peak removed. A three-dimensional difference-Fourier synthesis, phased only by the two molybdenum atoms ($R_F = 0.28$),[19] revealed the positions of all 27 of the remaining nonhydrogen atoms. Five cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms led to convergence with $R_F = 0.093$, $R_{wF^2} = 0.055$. A second difference-Fourier synthesis now showed evidence of anisotropic motion for many atoms and also indicated the positions of the six nonmethyl hydrogens. [Peak heights for these hydrogen atoms ranged from 0.4 to 0.8 e$^-$ Å^{-3}; this may be compared to values of 5.0–5.6 e$^-$ Å^{-3} for carbon atoms and 6.3–7.4 e$^-$ Å^{-3} for oxygen atoms on an "observed" Fourier synthesis.] Inclusion of these six hydrogen atoms in a structure-factor calculation led to a reduction in the discrepancy indices to $R_F = 0.091$, $R_{wF^2} = 0.053$.

Refinement was continued using anisotropic thermal parameters (T) in the form

$$T = \exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl)$$

Owing to a limitation in storage space in the IBM 7094 computer, parameters were divided into two submatrices which were refined in a single cycle. Matrix A contained the scale factor along with positional and anisotropic thermal parameters for Mo_1, Mo_2, O_1–O_3, C_1–C_3, C_9–C_{11}, and C_{16}–C_{18}; matrix B contained the corresponding parameters for O_4–O_6, C_4–C_8, C_{12}–C_{15}, and C_{19}–C_{21}. The six nonmethyl hydrogen atoms were included in calculated positions,[20] with $B = 6.0$ Å^2, and were not allowed to refine. After five cycles of least-squares refinement of positional and anisotropic thermal parameters, the suggested shifts were each less than $^1/_{20}$ of the appropriate standard deviation, and refinement was judged to be complete. The final discrepancy indices were $R_F = 0.076$ and $R_{wF^2} = 0.037$, and the standard error for an observation of unit weight was 1.73 (indicating an underestimate in the standard deviation of the intensity data). It should be noted that a Hamilton R-factor ratio test[21] indicates that the anisotropic refinement is meaningful at a level of confidence considerably better than 99.5%.

A final difference-Fourier synthesis showed no significant features, thus providing an independent check of the correctness of the structure. [Although there were miscellaneous peaks of height 0.2–0.4 e$^-$ within the vicinity of the methyl carbon atoms (C_{11}, C_{12}, C_{14}, C_{15}), no distinct C_{3v} patterns of methyl hydrogens could be distinguished. It is assumed then, that the methyl hydrogen atoms are undergoing substantially greater

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(15) $\bar{\mu}$ is the equiinclination angle, Υ the vertical Weissenberg coordinate,[16] and θ the Bragg angle.

(16) C. T. Prewitt, *Z. Krist.*, **13**, 355 (1960).

(17) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(18) All crystallographic calculations including Fourier syntheses, structure-factor calculations, least-squares refinement, distances–angles–planes calculations and atomic vibration ellipsoids were performed using CRYRM—an integrated set of crystallographic routines for the IBM 7094 written by R. E. Marsh and coworkers at the California Institute of Technology.

(19) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w||F_o|^2 - |F_c|^2|^2/\Sigma w|F_o|^4$.

(20) Hydrogen atom positions were calculated with $d(\text{C–H}) = 1.080$ Å and the appropriate angular geometry. They were recalculated at the end of the third, fourth, and fifth cycles of anisotropic refinement. "Shifts" were, however, small.

(21) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$[a]

H	K	FO	FC
L = 0			
4	0	1627	1594
6	0	1031	1031
8	0	266	233
10	0	146	112
3	1	453	397
4	1	2416	2139
6	1	1059	1200
7	1	737	725
8	1	962	975
9	1	651	631
10	1	656	698
11	1	600	635
3	2	1325	1368
4	2	904	769
5	2	1309	1337
6	2	534	469
7	2	860	844
9	2	159	121
11	2	119	76
2	3	213	192
3	3	680	572
4	3	183	175
5	3	611	402
6	3	263	218
7	3	494	482
8	3	261	222
9	3	395	434
10	3	133	165
11	3	360	371
0	4	216	116
1	4	343	313
2	4	251	152
4	4	174	144
5	4	262	256
6	4	193	171
7	4	367	354
8	4	167	160
9	4	185	154
10	4	126	159
1	5	146	107
2	5	343	278
4	5	748	769
5	5	227	168
6	5	690	651
8	5	461	626
9	5	181	133
10	5	489	477
0	6	1625	1522
1	6	1234	1212
2	6	1007	1025
3	6	1045	1006
4	6	1203	1192
5	6	923	902
6	6	1039	998
7	6	615	593
8	6	183	169
9	6	222	178
11	6	200	221
1	7	451	345
2	7	287	277
3	7	906	874
4	7	248	213
5	7	1123	1174
6	7	281	186
7	7	995	933
8	7	219	157
9	7	909	881
10	7	331	315
0	8	1075	1095
1	8	2170	2176
3	8	1042	1110
2	8	721	736
3	8	1057	1110
4	8	802	804
5	8	929	996
6	8	420	439
7	8	766	761
8	8	320	78
9	8	325	294
1	9	644	253
2	9	381	469
3	9	352	275
4	9	736	722
5	9	491	479
6	9	882	894
7	9	336	274
8	9	783	772
9	9	339	184
0	10	1180	1118
1	10	434	238
2	10	1012	1025
3	10	256	15
4	10	567	658
5	10	196	2
6	10	623	579
7	10	197	130
8	10	266	218
9	10	196	144
1	11	184	97
2	11	258	125
4	11	252	233
5	11	218	153
6	11	245	276
7	11	294	112
0	12	329	205
1	12	528	510
3	12	318	318
4	12	185	106
7	12	186	58
8	12	201	160
1	13	181	45
3	13	197	170
5	13	430	395
6	13	241	180
7	13	600	371
0	14	1023	1069
1	14	359	329
2	14	938	951
3	14	315	338
4	14	596	567
6	14	385	345
1	15	184	106
2	15	412	349
4	15	515	478
0	16	498	448
1	16	665	651
2	16	554	577
3	16	481	502
L = 1			
-11	0	708	745
-9	0	809	800
-7	0	521	573
-5	0	629	663
-3	0	589	573
3	0	368	401
5	0	1605	1608
7	0	991	991
9	0	837	819
11	0	635	661
-11	1	312	344
-10	1	455	467
-9	1	294	300
-8	1	462	672
-7	1	977	933
-6	1	1082	1146
-5	1	1402	1369
-4	1	1980	1857
-3	1	1528	1477
2	1	130	155
3	1	201	13
4	1	165	171
5	1	613	603
6	1	153	160
7	1	281	312
8	1	389	407
10	1	294	295
11	1	168	179
-11	2	312	364
-10	2	442	645
-9	2	429	417
-8	2	582	583
-7	2	797	845
-6	2	156	135
-5	2	1039	982
-4	2	511	461
-3	2	1489	1365
-2	2	611	701
2	2	235	247
3	2	938	748
4	2	1018	1036
5	2	263	218
6	2	905	950
7	2	361	409
8	2	677	726
9	2	229	186
10	2	493	535
11	2	202	180
-11	3	520	553
-10	3	165	129
-9	3	498	495
-8	3	267	266
-7	3	703	663
-6	3	814	795
-5	3	430	449
-4	3	811	770
-3	3	171	100
-2	3	375	326
-1	3	459	336
1	3	1020	801
2	3	288	250
3	3	451	519
4	3	501	508
5	3	1573	1543
6	3	654	686
7	3	990	1038
8	3	351	372
9	3	755	746
10	3	129	105
11	3	648	628
-11	4	191	163
-10	4	318	330
-9	4	365	408
-8	4	417	428
-7	4	790	791
-6	4	860	876
-5	4	1049	1044
-4	4	998	999
-3	4	608	595
-2	4	195	227
-1	4	674	484
0	4	1605	1638
1	4	731	656
2	4	854	913
3	4	524	513
4	4	956	958
5	4	536	451
6	4	501	494
7	4	169	140
8	4	134	113
9	4	224	200
10	4	151	13
11	4	191	149
-11	5	256	226
-10	5	287	290
-9	5	359	365
-8	5	279	317
-7	5	403	430
-6	5	205	113
-5	5	722	751
-4	5	388	343
-3	5	490	482
-2	5	196	144
-1	5	1094	1152
0	5	389	394
1	5	649	657
2	5	339	398
3	5	522	538
4	5	953	999
5	5	473	435
6	5	1067	1079
8	5	954	960
9	5	151	125
10	5	667	674
-11	6	158	164
-10	6	557	577
-9	6	282	277
-8	6	735	724
-6	6	457	450
-5	6	607	609
-4	6	143	170
-3	6	425	440
-2	6	293	320
-1	6	717	839
0	6	420	427
3	6	1038	1027
4	6	333	354
5	6	880	882
7	6	490	525
8	6	264	247
9	6	307	337
10	6	412	411
-10	7	572	623
-9	7	299	267
-8	7	760	795
-7	7	330	311
-6	7	1107	1141
-5	7	355	361
-4	7	1214	1278
-2	7	1293	1352
-1	7	153	72
0	7	1604	1636
2	7	1086	1144
4	7	950	980
6	7	713	723
7	7	357	358
9	7	175	182
-10	8	624	634
-9	8	278	263
-8	8	559	577
-7	8	271	186
-6	8	440	467
-4	8	214	168
-3	8	276	329
-2	8	302	313
0	8	706	595
1	8	829	846
2	8	291	336
3	8	374	346
4	8	802	822
5	8	294	341
6	8	805	810
7	8	375	350
8	8	570	555
9	8	191	171
10	8	638	681
-10	9	193	113
-9	9	502	467
-7	9	555	591
-6	9	435	443
-5	9	831	650
-4	9	343	301
-3	9	885	959
-2	9	751	788
-1	9	937	996
0	9	702	692
1	9	628	623
2	9	641	713
3	9	460	458
4	9	491	467
5	9	231	132
6	9	635	626
7	9	214	116
8	9	469	509
9	9	409	372
-9	10	365	274
-8	10	197	152
-7	10	294	314
-6	10	693	689
-5	10	276	283
-4	10	852	862
-2	10	706	726
-1	10	319	240
0	10	404	901
1	10	310	343
2	10	533	542
3	10	292	277
4	10	342	349
5	10	298	309
6	10	295	317
7	10	278	267
8	10	192	141
9	10	254	180
-8	11	253	297
-6	11	371	391
-4	11	259	256
-1	11	293	260
0	11	268	114
1	11	403	373
3	11	508	528
4	11	347	362
5	11	621	609
6	11	538	545
7	11	674	694
8	11	503	493
-7	12	416	442
-5	12	720	736
-4	12	175	53
-3	12	717	741
-1	12	862	866
1	12	670	635
2	12	190	210
3	12	398	370
4	12	234	157
7	12	177	0
-6	13	418	454
-4	13	420	441
-3	13	284	212
-2	13	442	457
-1	13	586	547
0	13	357	390
1	13	582	630
2	13	217	198
3	13	588	637
5	13	400	371
6	13	249	209
7	13	417	373
-6	14	207	148
6	14	220	267
-4	14	215	215
-2	14	249	223
-1	14	198	22
0	14	341	321
1	14	248	83
2	14	461	494
3	14	246	147
4	14	422	382
5	14	406	409
6	14	314	267
-5	15	646	673
-4	15	246	167
-3	15	742	784
-1	15	599	618
0	15	310	215
1	15	427	378
2	15	185	71
3	15	367	344
-1	16	216	5
0	16	306	272
L = 2			
-10	0	212	199
-8	0	311	346
-6	0	737	775
-4	0	731	666
-2	0	843	839
2	0	799	647
6	0	176	162
8	0	249	21
-11	1	166	160
-10	1	346	348
-8	1	466	483
-7	1	754	759
-6	1	400	415
-5	1	883	888
-4	1	656	403
-3	1	822	779
-2	1	377	319
1	1	419	568
2	1	710	553
3	1	213	153
4	1	134	69
5	1	176	117
6	1	205	212
7	1	207	5
8	1	234	223
9	1	204	218
10	1	238	253
11	1	192	166
-11	2	409	433
-10	2	286	302
-9	2	223	219
-8	2	393	422
-7	2	299	285
-6	2	150	40
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4	9	432	427
5	9	701	680
6	9	374	302
7	9	614	610
-8	10	150	155
-7	10	516	503
-6	10	206	251
-5	10	549	635
-3	10	558	574
-2	10	270	278
-1	10	414	309
1	10	523	544
2	10	449	440
3	10	441	422
4	10	261	240
5	10	167	176
-7	11	267	190
-6	11	236	199
-5	11	150	41
-4	11	268	277
-3	11	236	254
-2	11	189	277
-1	11	264	187
0	11	330	174
1	11	178	139
2	11	195	164
4	11	336	321
6	11	305	308
-7	12	252	178
-6	12	239	197
-3	12	272	242
-2	12	205	163
0	12	210	201
1	12	200	202
3	12	397	423
4	12	213	163
5	12	255	223
-5	13	245	232
-3	13	224	176
-2	13	350	329
0	13	275	264
1	13	165	125
2	13	254	253
3	13	169	36
4	13	461	463
-4	14	163	209
-3	14	457	490
-2	14	244	200
-1	14	463	472
1	14	645	583
L = 6			
-8	0	435	389
-6	0	336	34
-4	0	537	512
-2	0	832	807
0	0	1092	1073
2	0	640	663
4	0	635	626
6	0	403	367
8	0	324	321
-10	1	365	386
-9	1	265	257
-8	1	342	367
-7	1	343	348
-6	1	427	441
-5	1	308	302
-4	1	773	801
-2	1	607	744
0	1	808	776
2	1	296	322
3	1	183	182
4	1	321	322
5	1	414	409
7	1	436	446
-10	2	500	501
-8	2	656	691
-6	2	653	661
-5	2	578	535
-4	2	677	685
-3	2	669	597
-2	2	637	595
0	2	881	790
1	2	661	726
2	2	221	255
3	2	417	393
4	2	252	213
5	2	301	278
8	2	448	467
-10	3	374	351
-4	3	330	313
-3	3	615	525
-2	3	452	503
-1	3	496	563
0	3	943	918
1	3	786	861
2	3	1161	1215
3	3	539	579
4	3	1261	1228
5	3	375	417
6	3	953	982
7	3	273	203
8	3	810	827
-10	4	291	221
-9	4	476	454
-8	4	293	289
-7	4	415	633
-5	4	838	783
-4	4	851	833
-3	4	885	862
-2	4	593	612
-1	4	980	1021
0	4	641	649
1	4	706	718
2	4	423	451
3	4	276	275
6	4	271	228
7	4	337	358
8	4	244	224
-10	5	320	262
-9	5	209	174
-8	5	463	456
-7	5	167	198
-6	5	256	224
-5	5	412	414
-3	5	693	672
-2	5	211	45
-1	5	751	779
0	5	267	186
1	5	1329	1386
3	5	958	955
5	5	790	751
6	5	208	137
7	5	852	808
-9	6	381	350
-8	6	191	[illegible]
-7	6	544	489
-6	6	495	497
-5	6	600	631
-4	6	721	745
-3	6	479	427
-2	6	529	549
0	6	721	693
1	6	261	242
4	6	471	444
7	6	[illegible]	[illegible]
[illegible]	7	527	511
-8	7	191	189
-7	7	599	522
-5	7	489	493
-3	7	425	422
-1	7	443	461
0	7	422	399
3	7	196	74
6	7	299	316
-5	8	366	295
-3	8	227	145
-1	8	252	327
1	8	403	385
3	8	279	335
6	8	262	223
7	8	431	224
-8	9	445	466
-7	9	234	239
-6	9	554	513
-5	9	259	305
-4	9	318	315
-3	9	450	403
-1	9	395	405
1	9	294	282
3	9	423	417
4	9	338	250
5	9	372	350
6	9	240	152
-7	10	507	457
-5	10	375	440
-3	10	423	428
-1	10	403	494
1	10	414	424
2	10	247	226
3	10	226	268
-4	11	242	267
-3	11	203	269
-2	11	442	469
-1	11	352	365
0	11	431	406
1	11	460	449
2	11	596	625
3	11	606	654
4	11	565	534
-6	12	569	524
-4	12	462	464
-2	12	573	606
0	12	590	592
2	12	349	415
-4	13	279	144
-2	13	335	319
-1	13	265	36
0	13	509	517
2	13	641	656
L = 7			
-7	0	324	271
-5	0	265	195
-1	0	338	255
1	0	247	245
[illegible]	0	256	174
-10	1	282	264
-9	1	203	205
-8	1	236	273
-7	1	521	506
-6	1	390	382
-5	1	239	223
-3	1	450	476
-2	1	213	162
-1	1	472	505
1	1	332	340
2	1	200	184
4	1	415	405
-7	2	266	224
-6	2	266	331
-5	2	446	493
-4	2	241	256
-3	2	1166	1113
-2	2	329	297
-1	2	930	991
0	2	312	436
1	2	1014	1061
2	2	184	170
3	2	738	748
4	2	236	210
5	2	660	673
6	2	201	165
7	2	389	391
-10	3	194	151
-9	3	719	660
-8	3	338	342
-7	3	1102	1009
-5	3	871	814
-4	3	275	297
-3	3	611	611
-2	3	303	258
-1	3	443	465
0	3	568	522
3	3	522	453
5	3	602	513
7	3	504	511
-7	4	298	238
-5	4	484	496
-4	4	857	887
-3	4	583	593
-2	4	1173	1196
-1	4	620	661
0	4	1287	1274
1	4	754	713
2	4	909	902
3	4	688	663
4	4	729	715
6	4	603	635
7	4	320	353
-8	5	713	726
-6	5	938	839
-5	5	220	118
-4	5	847	842
-2	5	574	627
0	5	281	357
2	5	202	243
4	5	244	253
5	5	155	93
6	5	457	426
-9	6	218	12
-7	6	496	486
-5	6	742	732
-4	6	278	227
-3	6	623	691
-2	6	396	391
-1	6	415	357
0	6	651	623
1	6	442	345
4	6	539	552
6	6	456	405
-8	7	293	253
-7	7	277	260
-6	7	261	275
-3	7	319	195
3	7	208	47
4	7	230	165
-5	8	239	233
-4	8	262	223
-3	8	358	345
-1	8	242	211
4	8	215	162
-6	9	429	387
-4	9	356	256
-3	9	220	55
-2	9	327	324
1	9	263	264
3	9	189	213
-6	10	461	435
-4	10	654	655
-2	10	763	855
-1	10	206	25
0	10	646	665
2	10	628	575
3	10	226	276
4	10	678	631
-4	11	210	264
-3	11	328	293
-2	11	286	245
-1	11	312	210
1	11	232	98
-3	12	731	721
-1	12	942	977
1	12	604	864
L = 8			
-8	0	594	562
-6	0	721	705
-4	0	652	630
-2	0	1121	1130
0	0	1138	1060
2	0	568	585
4	0	571	521
6	0	320	315
-9	1	249	266
-8	1	258	148
-7	1	594	529
-6	1	376	357
-5	1	532	469
-3	1	256	231
-2	1	260	147
-1	1	351	374
2	1	639	546
3	1	233	229
4	1	542	538
5	1	468	415
6	1	399	468
-8	2	509	524
-7	2	475	438
-6	2	419	452
-5	2	409	394
-4	2	294	288
-3	2	578	598
-2	2	216	312
-1	2	630	691
1	2	644	636
3	2	451	419
4	2	254	117
5	2	475	489
6	2	218	173
-9	3	194	32
-8	3	280	269
-6	3	884	913
-2	3	691	685
-1	3	206	132
0	3	584	608
2	3	335	369
4	3	264	156
5	3	332	297
-9	4	245	219
-8	4	279	290
-7	4	303	270
-5	4	255	218
-4	4	268	147
0	4	207	184
1	4	321	303
3	4	304	274
4	4	291	53
5	4	250	295
6	4	245	191
-8	5	206	153
-7	5	392	329
-6	5	619	396
-5	5	631	621
-4	5	198	121
-1	5	425	432
1	5	448	487
2	5	319	308
3	5	350	355
-8	6	210	190
-7	6	437	424
-6	6	352	366
-5	6	241	253
-3	6	331	313
-1	6	381	405
0	6	323	262
1	6	319	309
4	6	477	474
-7	7	456	376
-6	7	318	241
-5	7	323	385
0	7	229	156
1	7	334	350
3	7	556	553
4	7	211	84
5	7	484	449
-7	8	481	465
-6	8	276	276
-5	8	418	404
-4	8	233	165
-3	8	553	489
-1	8	674	681
0	8	295	228
1	8	634	629
2	8	325	362
3	8	521	521
4	8	472	407
-6	9	364	353
-4	10	266	281
-2	10	346	342
0	10	356	384
1	10	253	236
-3	11	362	365
-2	11	385	387
-1	11	267	319
0	11	384	405
L = 9			
-7	0	548	459
-3	0	565	452
-1	0	435	444
1	0	[illegible]	[illegible]
3	0	1593	1585
5	0	690	714
-8	1	368	383
-7	1	812	755
-6	1	529	537
-5	1	697	675
-4	1	536	474
-3	1	801	617
-2	1	498	476
-1	1	627	737
0	1	470	417
1	1	379	373
2	1	212	55
3	1	277	265
-6	2	219	235
-4	2	254	193
-2	2	365	366
0	2	443	419
2	2	750	687
4	2	641	673
5	2	150	87
-5	3	217	172
-4	3	312	316
-2	3	351	[illegible]
4	3	234	268
-3	4	211	158
-2	4	198	242
0	4	194	248
1	4	206	103
4	4	278	35
-7	5	436	367
-5	5	431	389
-3	5	470	434
-2	5	211	286
-1	5	348	341
0	5	295	240
1	5	220	193
3	5	410	317
4	5	306	119
-3	6	207	143
1	6	424	424
3	6	510	499
-6	7	655	615
-4	7	657	659
-1	7	187	144
0	7	713	683
3	7	257	106
-3	8	227	75
0	8	354	372
1	8	366	349
2	8	613	550
-4	9	262	266
-3	9	633	578
-2	9	370	432
-1	9	568	570
0	9	236	286
1	9	418	377
L = 10			
-6	0	629	638
-4	0	440	421
-2	0	283	320
0	0	387	287
-5	1	277	198
-3	1	382	416
-2	1	315	357
-1	1	422	497
0	1	409	350
1	1	344	368
2	1	461	466
3	1	256	190
-5	2	196	248
-4	2	332	359
-2	2	544	495
0	2	232	289
2	2	373	308
-4	3	327	335
-2	3	450	396
0	3	510	438
2	3	204	111
-4	4	222	209
-3	4	384	332
-2	4	322	368
-1	4	321	332
0	4	251	210
1	4	327	332
2	4	263	234
-5	5	276	251
-1	5	290	423
0	5	326	250
1	5	362	275
-3	6	344	347
1	6	248	266
-1	7	374	319
L = 11			
-3	0	182	82
-2	1	232	269
-1	1	270	159
-1	1	270	159

[a] Table shows h, k, $|10F_o|$, and $|10F_c|$ in blocks of constant l.

thermal motion than the other hydrogen atoms in the molecule.]

Throughout the analysis, scattering factors for neutral molybdenum, oxygen, carbon, and hydrogen (as compiled by Ibers[22a]) were used. Dispersion corrections[22b] are small ($\Delta f'_{Mo} = -1.7$ e$^-$; $\Delta f''_{Mo} = +0.9$ e$^-$) and were ignored, since our version of CRYRM[18] had no facility for such a calculation.

The residual minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$. Final observed and calculated structure factors are shown in Table I. Positional and thermal parameters are collected in Table II. Atomic vibration ellipsoids (for nonhydrogen atoms) are defined in Table III.

The Molecular Structure

Figure 1 shows the molecule projected down "b." Interatomic distances (with esd's) are collected in

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[22] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) pp 202, 211; (b) p 216.

TABLE II

FINAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS (×10⁴) FOR $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$, WITH ESD'S[a]

ATOM	X	Y	Z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
MO1	0.22576(10)	0.08245(8)	-0.18032(14)	50.0(1.2)	32.1(0.7)	75.9(1.9)	-2.0(1.3)	14.4(2.1)	-1.5(1.6)
MO2	0.23041(9)	0.21313(8)	0.04574(13)	49.2(1.1)	28.9(0.7)	76.9(1.9)	-2.3(1.2)	21.1(2.1)	-4.2(1.5)
O1	0.1997(11)	0.2126(8)	-0.3867(14)	132(14)	37(7)	123(19)	-2(15)	53(26)	44(18)
O2	0.1301(12)	-0.0370(9)	-0.3940(14)	154(16)	53(7)	105(19)	-66(18)	-18(27)	-34(19)
O3	-0.0308(11)	0.0667(11)	-0.1524(16)	65(12)	137(13)	214(25)	-91(17)	130(26)	-185(26)
O4	-0.0227(11)	0.1711(10)	0.0712(14)	58(11)	110(11)	171(24)	-69(17)	58(23)	-76(24)
O5	0.1575(12)	0.3630(8)	0.1819(15)	147(15)	44(8)	146(21)	48(16)	53(28)	-59(18)
O6	0.1635(11)	0.3286(9)	-0.1806(14)	124(14)	53(8)	113(20)	35(16)	28(25)	51(20)
C1	0.3326(11)	-0.0134(9)	-0.0442(16)	44(12)	23(7)	70(20)	5(14)	5(24)	-7(18)
C2	0.3845(12)	-0.0038(11)	-0.1520(17)	36(11)	42(9)	96(23)	27(16)	32(26)	-15(22)
C3	0.4271(12)	0.0747(10)	-0.1554(18)	47(12)	27(8)	107(24)	13(16)	39(27)	-25(21)
C4	0.4233(10)	0.2039(10)	-0.0215(16)	30(10)	39(8)	72(21)	-26(15)	40(24)	0(22)
C5	0.4268(12)	0.2406(10)	0.0955(20)	45(12)	28(8)	110(27)	-9(16)	-26(29)	8(23)
C6	0.3833(11)	0.2130(11)	0.2004(18)	25(11)	49(10)	97(24)	-14(17)	3(27)	21(23)
C7	0.3248(11)	0.1402(10)	0.2173(16)	48(11)	36(9)	44(19)	-9(16)	28(24)	-8(20)
C8	0.2908(11)	0.0809(8)	0.1278(15)	50(11)	13(6)	65(19)	5(13)	14(24)	14(18)
C9	0.3370(10)	0.0633(9)	0.0177(15)	26(10)	23(7)	62(19)	0(13)	-32(22)	-15(18)
C10	0.3988(11)	0.1167(10)	-0.0518(17)	31(11)	29(7)	107(24)	-24(15)	-21(25)	58(23)
C11	0.2797(12)	-0.0935(9)	0.0001(17)	56(12)	24(7)	127(25)	-47(15)	-3(27)	19(20)
C12	0.4611(14)	0.2566(10)	-0.1259(18)	88(15)	30(8)	104(25)	0(17)	109(32)	9(21)
C13	0.2908(15)	0.1335(11)	0.3470(18)	107(17)	42(10)	59(23)	-26(21)	-43(31)	13(22)
C14	0.1848(18)	0.0785(12)	0.3490(19)	150(22)	42(10)	100(26)	6(23)	127(39)	-15(24)
C15	0.3932(17)	0.0894(16)	0.4362(21)	102(19)	116(18)	90(27)	-39(28)	-59(36)	73(34)
C16	0.2062(14)	0.1671(12)	-0.3066(20)	79(15)	33(9)	104(27)	-8(19)	-4(32)	18(25)
C17	0.1668(14)	0.0082(11)	-0.3160(19)	77(15)	32(8)	98(26)	-21(19)	-1(30)	8(24)
C18	0.0613(15)	0.0767(11)	-0.1569(19)	47(15)	54(10)	134(28)	-32(18)	7(31)	-78(24)
C19	0.0681(15)	0.1801(11)	0.5836(18)	61(16)	47(10)	102(26)	7(20)	-20(30)	-34(24)
C20	0.1850(14)	0.3079(12)	0.1316(18)	87(15)	36(9)	92(25)	40(20)	38(30)	-11(24)
C21	0.1868(13)	0.2839(11)	-0.0998(21)	56(13)	25(8)	141(30)	26(17)	47(31)	3(25)
H2	0.3907	-0.0495	-0.2217						
H3	0.4732	0.0984	-0.2253						
H5	0.4695	0.2990	0.1059						
H6	0.3968	0.2536	0.2792						
H8	0.2196	0.0440	0.1456						
H13	0.2709	0.1948	0.3726						

[a] Esd's appear in parentheses after each parameter. They are right-adjusted to the last significant digit of the preceding number.

TABLE III

ATOMIC VIBRATION ELLIPSOIDS[a,b] FOR $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$

ATOM	BMAX	D.C.'S	BMED	D.C.'S	BMIN	D.C.'S
MO1	3.61	(-225,-220, 973)	3.45	(-159, 969, 211)	2.71	(961, 108, 94)
MO2	3.64	(-32,-268, 956)	3.08	(-185, 949, 284)	2.66	(-982,-169, 80)
O1	7.23	(944, 57, 167)	6.59	(-307, 510, 843)	2.99	(-120,-858, 512)
O2	10.22	(-895, 431, 259)	6.27	(-209,-635, 768)	2.97	(394, 641, 586)
O3	19.84	(172,-806, 531)	5.39	(-10, 574, 810)	2.32	(-985,-146, 249)
O4	13.66	(193,-884, 389)	6.76	(-192, 392, 919)	2.42	(-962,-255, 63)
O5	9.33	(-771,-525, 480)	7.50	(525,-203, 731)	2.66	(-361,-827, 485)
O6	7.06	(622, 657, 320)	6.48	(-744, 327, 695)	3.44	(242,-680, 644)
C1	3.54	(-412,-284, 921)	2.45	(543, 686, 389)	2.24	(732,-669, 8)
C2	5.24	(-259,-808, 564)	4.20	(257, 471, 791)	1.44	(-931, 355, 236)
C3	5.32	(-15,-342, 930)	3.15	(683, 683, 146)	1.82	(-730, 646, 339)
C4	4.55	(312,-941, 77)	3.44	(126, 176, 943)	0.86	(-942,-288, 323)
C5	5.88	(-440, -42, 956)	3.11	(352,-927, 71)	1.96	(826, 373, 284)
C6	5.96	(-204, 823, 557)	4.08	(-74,-553, 831)	1.31	(976, 130, 14)
C7	4.00	(242,-951, 152)	2.59	(852, 304, 284)	1.83	(-465, 61, 947)
C8	3.20	(-213, 245, 968)	2.73	(972, 154, 20)	1.24	(102,-957, 251)
C9	3.92	(-506,-334, 867)	2.38	(-304, 932, 244)	0.93	(807, 142, 435)
C10	7.00	(-349, 523, 824)	1.95	(435,-645, 550)	1.18	(-830,-558, 137)
C11	6.77	(-446, 342, 889)	4.08	(623,-545, 453)	0.95	(-643,-766, 74)
C12	6.53	(638, 62, 654)	3.27	(-265, 954, 184)	2.40	(-723,-295, 734)
C13	7.48	(-868, 378, 457)	4.06	(-367,-925, 155)	2.17	(334, -34, 876)
C14	8.90	(862, -1, 362)	4.78	(-190,-928, 348)	2.97	(-471, 373, 865)
C15	14.00	(-312, 899, 353)	6.32	(-834,-414, 494)	2.64	(454,-142, 794)
C16	5.66	(-568, 331, 835)	3.96	(807, 44, 451)	3.23	(-162,-943, 315)
C17	5.61	(-694, 363, 726)	3.96	(471,-425, 687)	2.95	(545, 830, 35)
C18	8.85	(-13,-677, 728)	4.23	(-625, 579, 617)	1.80	(780, 453, 299)
C19	6.65	(-393,-625, 729)	4.06	(-498, 761, 491)	2.80	(773, 172, 477)
C20	5.93	(-783,-622, 149)	4.42	(177,-187, 925)	2.50	(-597, 761, 349)
C21	6.58	(46, 43, 977)	3.79	(-745,-664, 183)	1.85	(-666, 746, 106)

[a] Direction cosines (dc's) for the major, median, and minor axes of the vibration ellipsoid are defined relative to the axes of the monoclinic cell. The dc's have been multiplied by 1000. [b] Atomic vibration ellipsoids are presented in terms of the isotropic thermal parameter B, which may be related to the root-mean-square displacement, $(\overline{u^2})^{1/2}$ by $(\overline{u^2})^{1/2} = [B/8\pi^2]^{1/2}$.

able IV; bond angles and their esd's are given in Table V.

The molecule has an over-all *cis* configuration—*i.e.*, the two $Mo(CO)_3$ groups are bonded to the same side of the guaiazulene ligand. [A similar stereochemistry is observed for the unsubstituted complex, $C_{10}H_8Mo_2(CO)_6$.[13,14]] One $Mo(CO)_3$ group is associated with all carbon atoms in the five-membered ring, which may be regarded as a trisubstituted π-cyclopentadienyl system. The second $Mo(CO)_3$ group is within bonding range of the five remaining atoms of the azulene nucleus (*i.e.*, all atoms of the seven-membered ring except for the two "fused" atoms C_9 and C_{10}) and may be considered as participating in a *noncyclic* π-pentadienyl→metal

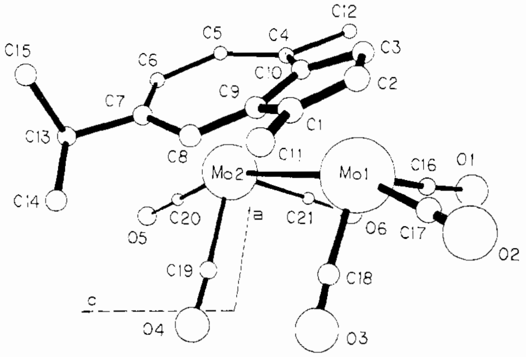
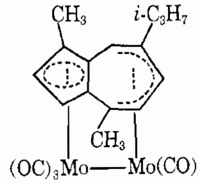


Figure 1.—Guaiazulenedimolybdenum hexacarbonyl, viewed down "*b*." (Hydrogen atoms are omitted for clarity.)

linkage. The donation of six electrons from the π-cyclopentadienyl anion, six electrons from the π-pentadienyl anion, and two electrons from each of the carbonyl ligands gives each of the d^5 Mo(I) ions a configuration one electron short of the appropriate inert-gas configuration;[23] the molybdenum–molybdenum distance of 3.267 ± 0.006 Å is indicative of a metal–metal bond, each molybdenum atom then obtaining the xenon configuration, in keeping with the observed diamagnetism of the complex.[24] The molecule may be formally described by II.



II

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[23] This enumeration of electrons may, of course, be accomplished in an equally satisfactory manner by considering π-cyclopentadienyl and π-pentadienyl ligands as neutral, five-electron donors bonded to molybdenum in the zerovalent state. The difference is simply one of formalism.

[24] The initial report[1] that the parent molecule, $C_{10}H_8Mo_2(CO)_6$, was paramagnetic was found later[3] to be in error.

TABLE IV

INTERATOMIC DISTANCES WITHIN THE $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$ MOLECULE WITH ESD'S[a]

Atoms	Dist, Å	Atoms	Dist, Å
(i) Distances from Molybdenum Atoms			
Mo_1-Mo_2	3.267 (06)		
Mo_1-C_1	2.381 (15)	Mo_2-C_4	2.510 (15)
Mo_1-C_2	2.329 (17)	$Mo-C_5$	2.340 (17)
Mo_1-C_3	2.355 (16)	Mo_2-C_6	2.268 (17)
Mo_1-C_{10}	2.356 (16)	Mo_2-C_7	2.350 (15)
Mo_1-C_9	2.367 (14)	Mo_2-C_8	2.409 (14)
$Mo_1\cdots C_4$	3.336 (15)	$Mo_2\cdots C_9$	2.799 (14)
$Mo_1\cdots C_8$	3.337 (14)	$Mo_2\cdots C_{10}$	2.879 (16)
Mo_1-C_{16}	1.946 (19)	Mo_2-C_{19}	2.019 (18)
Mo_1-C_{17}	1.959 (18)	Mo_2-C_{20}	1.936 (19)
Mo_2-C_{18}	2.003 (19)	Mo_2-C_{21}	1.971 (19)
$Mo_1\cdots O_1$	3.086 (14)	$Mo_2\cdots O_4$	3.126 (15)
$Mo_1\cdots O_2$	3.120 (14)	$Mo_2\cdots O_5$	3.068 (14)
$Mo_1\cdots O_3$	3.107 (16)	$Mo_2\cdots O_6$	3.116 (14)
(ii) Distances around π-Cyclopentadienyl and π-Pentadienyl Systems			
C_1-C_2	1.423 (22)	C_4-C_5	1.410 (22)
C_2-C_3	1.384 (23)	C_5-C_6	1.405 (24)
C_3-C_{10}	1.413 (23)	C_6-C_7	1.405 (23)
$C_{10}-C_9$	1.434 (21)	C_7-C_8	1.394 (21)
C_9-C_1	1.424 (20)		
(iii) Other Distances within the Guaiazulene Ligand			
C_4-C_{10}	1.485 (22)	C_7-C_{13}	1.541 (23)
C_8-C_9	1.430 (20)	$C_{13}-C_{14}$	1.547 (27)
C_1-C_{11}	1.564 (22)	$C_{13}-C_{15}$	1.599 (29)
C_4-C_{12}	1.554 (23)		
(iv) Carbon–Oxygen Distances			
$C_{16}-O_1$	1.143 (24)	$C_{19}-O_4$	1.115 (24)
$C_{17}-O_2$	1.160 (23)	$C_{20}-O_5$	1.131 (23)
$C_{18}-O_3$	1.110 (25)	$C_{21}-O_6$	1.147 (23)
(v) Contacts between Carbonyl Groups			
$O_1\cdots O_2$	4.172 (20)	$O_4\cdots O_5$	3.882 (21)
$O_2\cdots O_3$	3.890 (21)	$O_5\cdots O_6$	4.022 (21)
$O_3\cdots O_1$	4.688 (21)	$O_6\cdots O_4$	4.591 (22)
$C_{16}\cdots C_{17}$	2.644 (26)	$C_{19}\cdots C_{20}$	2.565 (26)
$C_{17}\cdots C_{18}$	2.560 (26)	$C_{20}\cdots C_{21}$	2.569 (26)
$C_{18}\cdots C_{16}$	2.953 (27)	$C_{21}\cdots C_{19}$	2.941 (26)
$O_1\cdots O_6$	3.033 (20)	$C_{16}\cdots C_{21}$	3.002 (27)
$O_3\cdots O_4$	2.975 (22)	$C_{18}\cdots C_{19}$	2.894 (26)
(vi) Contacts between Azulene and Carbonyl Ligands			
$C_9\cdots C_{18}$	3.508 (24)	$C_4\cdots C_{21}$	3.080 (24)
$C_1\cdots C_{18}$	3.564 (24)	$C_5\ldots C_{21}$	3.341 (25)
$C_1\cdots C_{17}$	3.308 (24)	$C_5\cdots C_{20}$	3.146 (25)
$C_2\cdots C_{17}$	2.897 (25)	$C_6\cdots C_{20}$	2.812 (25)
$C_3\cdots C_{17}$	3.464 (25)	$C_7\ldots C_{20}$	3.265 (24)
$C_3\cdots C_{16}$	3.233 (25)	$C_7\cdots C_{19}$	3.310 (24)
$C_{10}\cdots C_{16}$	3.405 (25)	$C_8\cdots C_{19}$	3.082 (23)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number. Except for the Mo_1-Mo_2 bond, they do not include any contribution from errors in the unit-cell dimensions (which are possibly as great as 1 part in 550). The esd on the Mo_1-Mo_2 bond is only 0.001 Å from the correlation matrix; this has been increased to 0.006 Å to allow for possible errors in cell constants. Esd's for other bond lengths will not be so drastically affected on correction for possible cell errors.

TABLE V

ANGLES WITHIN THE $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$ MOLECULE, WITH ESD'S[a]

Atoms	Angle, deg	Atoms	Angle, deg
(i) Around Molybdenum Atoms			
$C_1-Mo_1-C_2$	35.2 (0.7)	$C_4-Mo_2-C_5$	33.6 (0.7)
$C_2-Mo_1-C_3$	34.4 (0.7)	$C_5-Mo_2-C_6$	35.5 (0.7)
$C_3-Mo_1-C_{10}$	34.9 (0.7)	$C_6-Mo_2-C_7$	35.4 (0.7)
$C_{10}-Mo_1-C_9$	35.4 (0.7)	$C_7-Mo_2-C_6$	34.0 (0.7)
$C_9-Mo_1-C_1$	34.9 (0.7)	$C_8-Mo_2-C_4$	80.0 (0.7)
$Mo_2-Mo_1\cdots O_1$	95.1 (0.3)	$Mo_1-Mo_2\cdots O_4$	91.3 (0.3)
$Mo_2-Mo_1-C_{16}$	93.2 (0.6)	$Mo_1-Mo_2-C_{19}$	88.6 (0.5)
$Mo_2-Mo_1-\cdots O_2$	160.0 (0.3)	$Mo_1-Mo_2\cdots O_5$	157.1 (0.3)
$Mo_2-Mo_1\cdots C_{17}$	160.4 (0.6)	$Mo_1-Mo_2-C_{20}$	157.2 (0.6)
$Mo_2-Mo_1\cdots O_3$	83.0 (0.3)	$Mo_1-Mo_2\cdots O_6$	79.9 (0.3)
$Mo_2-Mo_1-C_{18}$	80.3 (0.5)	$Mo_1-Mo_2-C_{21}$	78.6 (0.6)
$O_1\cdots Mo_1\cdots O_2$	84.5 (0.4)	$O_4\cdots Mo_2\cdots O_5$	77.6 (0.4)
$C_{16}-Mo_1-C_{17}$	85.2 (0.8)	$C_{19}-Mo_2-C_{20}$	80.9 (0.8)
$O_1\cdots Mo_1\cdots O_3$	98.4 (0.4)	$O_4\cdots Mo_2\cdots O_6$	94.6 (0.4)
$C_{16}-Mo_1-C_{18}$	96.8 (0.8)	$C_{19}-Mo_2-C_{21}$	94.9 (0.8)
$O_2\cdots Mo_1\cdots O_3$	77.3 (0.4)	$O_5\cdots Mo_2\cdots O_6$	81.1 (0.4)
$C_{17}-Mo_1-C_{18}$	80.5 (0.8)	$C_{20}-Mo_2-C_{21}$	82.2 (0.8)
(ii) Within Carbonyl Ligands			
$Mo_1-C_{16}-O_1$	174.2 (1.7)	$Mo_2-C_{19}-O_4$	171.5 (1.7)
$Mo_1-C_{17}-O_2$	177.9 (1.7)	$Mo_2-C_{20}-O_5$	179.4 (1.7)
$Mo_1-C_{18}-O_3$	172.6 (1.7)	$Mo_2-C_{21}-O_6$	176.3 (1.7)
(iii) Angles within the Azulene Nucleus			
$C_9-C_1-C_2$	108.0 (1.3)	$C_{10}-C_4-C_5$	126.1 (1.4)
$C_1-C_2-C_3$	109.4 (1.5)	$C_4-C_5-C_6$	130.1 (1.6)
$C_2-C_3-C_{10}$	107.2 (1.5)	$C_5-C_6-C_7$	129.3 (1.6)
$C_3-C_{10}-C_9$	109.6 (1.4)	$C_6-C_7-C_8$	126.3 (1.5)
$C_{10}-C_9-C_1$	105.6 (1.3)	$C_7-C_8-C_9$	128.8 (1.4)
		$C_8-C_9-C_{10}$	128.3 (1.3)
$C_1-C_9-C_8$	126.1 (1.3)	$C_9-C_{10}-C_4$	124.5 (1.4)
$C_3-C_{10}-C_4$	125.8 (1.4)		
(iv) Angles for Substituents on the Azulene Ligand			
$C_9-C_1-C_{11}$	125.4 (1.3)	$C_6-C_7-C_{13}$	112.9 (1.4)
$C_2-C_1-C_{11}$	126.6 (1.4)	$C_8-C_7-C_{13}$	120.6 (1.4)
$C_{10}-C_4-C_{12}$	116.0 (1.3)	$C_7-C_{13}-C_{14}$	112.8 (1.5)
$C_5-C_4-C_{12}$	117.5 (1.4)	$C_7-C_{13}-C_{15}$	108.1 (1.5)
		$C_{14}-C_{13}-C_{15}$	105.2 (1.5)

[a] See footnote *a*, Table IV.

The Guaiazulene Ligand

The guaiazulene ligand maintains its essential chemical identity as a system containing fused, delocalized five- and seven-membered rings, but the π-cyclopentadienyl→Mo_1 and π-pentadienyl→Mo_2 bonding leads to some carbon–carbon bond lengths around the azulene nucleus that differ significantly from those in the parent hydrocarbon.[25-28] Figure 2 compares bond lengths within the azulene nuclei of guaiazulenedimolybdenum hexacarbonyl, azulene-1,3-dipropionic acid,[27] and the molecular complex azulene–1,3,5-trinitrobenzene.[28] Specifically it can be seen that the main differences in bond length between the free and the coordinated hydrocarbon involve the C_4-C_{10}, C_8-C_9, and C_9-C_{10} bonds. There appear to be no great differences in bond angle between the azulene nuclei in the present metal complex and in the uncoordinated species.

Within the limits of experimental error, distances

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(25) Azulene crystallizes in a disordered manner,[26] thus precluding the accurate determination of bond lengths. However, bond lengths *are* available for the ordered azulene-1,3-dipropionic acid[27] and the slightly disordered azulene–1,3,5-trinitrobenzene molecular complex.[22]

(26) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).

(27) H. L. Ammon and M. Sundaralingam, *J. Am. Chem. Soc.*, **88**, 4794 (1966).

(28) A. W. Hanson, *Acta Cryst.*, **19**, 19 (1965).

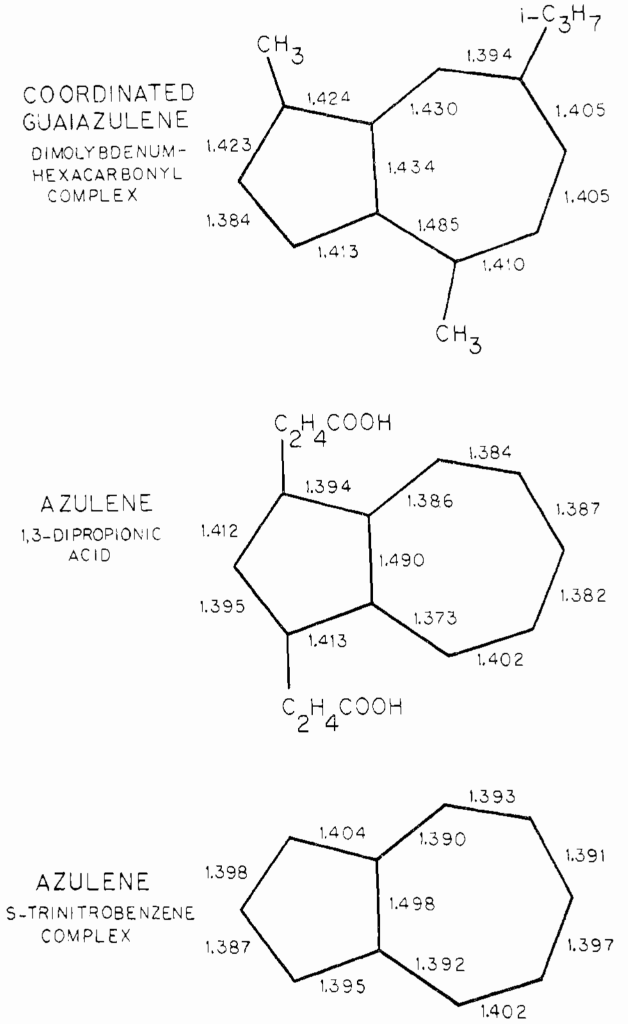

Figure 2.—A comparison of bond lengths for the azulene nuclei in (a) $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$, (b) $(HOOCCH_2CH_2)_2C_{10}H_6$, and (c) $C_{10}H_8$–*sym*-$C_6H_3(NO_2)_3$.

around the π-cyclopentadienyl system are consistent with precise D_{5h} local symmetry; individual carbon–carbon bond lengths range from 1.384 ± 0.023 to 1.434 ± 0.021 Å and average 1.418 Å, bond angles vary from 105.6 ± 1.3 to 109.6 ± 1.4° and average 108.0°, and the root-mean-square deviation from planarity is 0.015 Å (see Table VI). The appropriate molybdenum atom, Mo_1, lies −2.027 Å from the π-cyclopentadienyl system (the negative sign may be regarded simply as a direction indicator) while the three substituents (C_4, C_8, and C_{11}) are, respectively −0.030, −0.041, and +0.091 Å out of the plane of the five-membered ring. Individual molybdenum–carbon distances for the π-cyclopentadienyl system range from 2.329 ± 0.017 to 2.381 ± 0.015 Å, averaging 2.358 Å.

The second molybdenum atom, Mo_2, is bonded to atoms C_4 through C_8 *via* a π-pentadienyl→metal linkage, with individual molybdenum–carbon bond lengths being: Mo_2–C_4, 2.510 ± 0.015 Å; Mo_2–C_5, 2.340 ± 0.017 Å; Mo_2–C_6, 2.268 ± 0.017 Å; Mo_2–C_7, 2.350 ± 0.015 Å; Mo_2–C_8, 2.409 ± 0.014 Å. [The "fused" carbon atoms, C_9 and C_{10}, are 2.799 ± 0.014 and 2.879 ± 0.015 Å, respectively, from Mo_2. Since they are already involved in bonding to Mo_1 (at distances 2.367 ± 0.014 and 2.356 ± 0.016 Å), it is unlikely that they will participate to any appreciable extent in the bonding to Mo_2.] Molybdenum–carbon distances vary systematically around the π-pentadienyl system, the longest values being for the "terminal" carbon atoms (C_4 and C_8) and the shortest being for the "central" atom (C_6). [This pattern appears to be characteristic of π-pentadienyl systems, since similar features have previously been noted for hexamethylcyclohexadienylrhenium tricarbonyl[29] and azulenedimanganese hexacarbonyl.[6]] The π-pentadienyl ligand is approximately planar (rms deviation = 0.016 Å): Mo_2 lies −1.797 Å from this plane while deviations of the substituents are: $\delta(C_9)$ = +0.352 Å, $\delta(C_{10})$ = +0.397 Å, $\delta(C_{12})$ = −0.238 Å, $\delta(C_{13})$ = +0.003 Å. Carbon–carbon distances around the π-pentadienyl system vary from 1.394 ± 0.021 to 1.410 ± 0.022 Å, averaging 1.403 Å. Although this mean value is only 0.015 Å less than the mean interatomic distance around the π-cyclopentadienyl ring, it *could* be indicative of stronger carbon–carbon bonding within the noncyclic delocalized system. This would be in keeping with the fact that the π-cyclopentadienyl→Mo_1 bonding is stronger than the π-pentadienyl→Mo_2 bonding. [Evidence for this comes both from this crystallographic analysis *via* a consideration of molybdenum–carbon

Table VI

Important Least-Squares Planes[a] Within the $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$ Molecule

(i) π-Cyclopentadienyl Plane:

$0.7924X - 0.2812Y + 0.5412Z = 2.9606^{b}$

C_1*	+0.021 (15)	C_4	−0.030 (15)
C_2*	−0.016 (17)	C_5	+0.353 (17)
C_3*	+0.006 (16)	C_6	+0.540 (17)
C_{10}*	+0.007 (16)	C_7	+0.402 (15)
C_9*	−0.017 (14)	C_8	−0.041 (14)
Mo_1	−2.027 (1)	C_{11}	+0.091 (16)

(ii) π-Pentadienyl Plane:

$0.8200X - 0.4769Y + 0.3162Z = 2.4547^{b}$

C_4*	+0.012 (15)	C_1	+0.787 (15)
C_5*	−0.011 (17)	C_2	+1.003 (17)
C_6*	−0.010 (17)	C_3	+0.796 (16)
C_7*	+0.025 (15)	C_9	+0.352 (14)
C_8*	−0.017 (14)	C_{10}	+0.397 (16)
Mo_2	−1.797 (1)	C_{12}	−0.238 (18)
		C_{13}	+0.003 (18)

(iii) $0.7836X - 0.2655Y + 0.5616Z = 2.9365^{b}$

C_4*	−0.003 [15)	C_1	−0.004 (15)
C_8*	+0.004 (14)	C_2	−0.069 (17)
C_9*	−0.008 (14)	C_3	−0.033 (16)
C_{10}*	+0.007 (16)	C_5	+0.417 (17)
		C_6	+0.626 (17)
		C_7	+0.480 (15)
		C_{11}	+0.062 (16)

[a] Planes are derived using unit weights for atoms with asterisks and zero weights for all other atoms. [b] Planes are defined in terms of the orthogonalized coordinates X, Y, Z. These are related to the monoclinic cell coordinates by: $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$.

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(29) (a) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967); (b) P. H. Bird and M. R. Churchill, unpublished work.

distances and from chemical studies[5] in which it has been shown that the π-pentadienyl→molybdenum bond is preferentially cleaved by sodium, giving the dimeric 4-*exo*-4′-*exo*-[AzMo(CO)$_3$$^-$]$_2$ dianion.[30]

There is one problem remaining with respect to the observed π-pentadienyl–Mo$_2$ distances, and this involves the unexpected difference of 0.101 Å (*i.e.*, 6.7σ) between the Mo$_2$–C$_4$ and Mo$_2$–C$_8$ bond lengths. There appears to be no *rationale* for this phenomenon in terms of *inter*molecular repulsions (see Table VII) and it must therefore result from *intra*molecular forces. Figure 3 shows the molecule projected onto the plane of the π-cyclopentadienyl ligand and (ignoring methyl and isopropyl groups) it can be seen that the molecule *could* possess a mirror plane containing O$_5$, C$_{20}$, C$_6$, Mo$_2$ Mo$_1$, C$_2$, C$_{17}$, and O$_2$. In practice, however, this would-be mirror plane is not utilized and the "backbone" of the molecule, as defined by O$_5$–C$_{20}$–Mo$_2$–Mo$_1$–C$_{17}$–O$_2$, shows a discernible zigzag pattern. In addition to the Mo$_2$–C$_4$ distance being about 0.1 Å longer than the Mo$_2$–C$_8$ bond length, there is also a significant difference (0.080 Å, representing ~5.3σ) in the Mo$_2$···C$_9$ and Mo$_2$···C$_{10}$ contacts, with the atom lying next to C$_4$ (*i.e.*, C$_{10}$) being the more distant from Mo$_2$. It seems probable[31] that these significant asymmetries result from a general pattern of strain in the molecule caused by a combination of: (i) simultaneous requirements for π-cyclopentadienyl→Mo$_1$, π-pentadienyl→Mo$_2$, and Mo$_1$–Mo$_2$ bonding and (ii) intramolecular oxygen–oxygen repulsions (O$_1$···O$_6$, 3.033 ± 0.020 Å; O$_3$···O$_4$, 2.975 ± 0.022 Å).

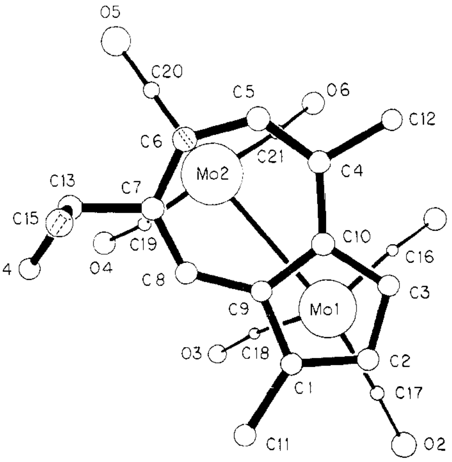

Figure 3.—Guaiazulenedimolybdenum hexacarbonyl, projected onto the least-squares plane through the five-membered ring.

TABLE VII

INTERMOLECULAR CONTACTS WITHIN THE (*i*-C$_3$H$_7$)(CH$_3$)$_2$C$_{10}$H$_5$Mo$_2$(CO)$_6$ CRYSTAL (TO 3.5 Å)

Atoms	Dist, Å	Atoms	Dist, Å
O$_1$···C$_5$ (III)	3.29	C$_6$···O$_6$ (VI)	3.43
O$_1$···C$_1$ (VIII)	3.43	C$_{11}$···O$_1$ (VII)	3.43
O$_1$···H$_5$ (III)	2.72	C$_{11}$···O$_4$ (I)	3.27
O$_2$···O$_6$ (VII)	3.29	C$_{16}$···H$_5$ (III)	2.86
O$_3$···H$_5$ (III)	3.44	C$_{18}$···H$_5$ (III)	3.34
O$_3$···H$_6$ (III)	3.12	C$_{18}$···H$_6$ (III)	3.40
O$_3$···H$_8$ (I)	2.89	C$_{21}$···H$_2$ (VIII)	3.40
O$_4$···C$_{11}$ (I)	3.27	H$_2$···O$_6$ (VII)	2.31
O$_4$···H$_6$ (III)	3.42	H$_2$···C$_{21}$ (VII)	3.40
O$_5$···H$_3$ (V)	2.63	H$_3$···O$_5$ (IV)	2.63
O$_6$···O$_2$ (VIII)	3.29	H$_5$···O$_1$ (VI)	2.72
O$_6$···C$_2$ (VIII)	3.30	H$_5$···O$_3$ (VI)	3.44
O$_6$···C$_6$ (III)	3.43	H$_5$···C$_{16}$ (VI)	2.86
O$_6$···H$_2$ (VIII)	2.31	H$_5$···C$_{18}$ (VI)	3.34
O$_6$···H$_6$ (III)	3.39	H$_6$···O$_3$ (VI)	3.12
C$_1$···C$_3$ (II)	3.44	H$_6$···O$_4$ (VI)	3.42
C$_2$···O$_6$ (VII)	3.30	H$_6$···O$_6$ (VI)	3.39
C$_3$···C$_1$ (II)	3.44	H$_6$···C$_{18}$ (VI)	3.40
C$_5$···O$_1$ (VI)	3.29	H$_8$···O$_3$ (I)	2.89

Transformations for above Atoms

I	$-x$	$-y$	$-z$
II	$-x + 1$	$-y$	$-z$
III	$x - {}^1/_2$	$-y + {}^1/_2$	$z - {}^1/_2$
IV	$x + {}^1/_2$	$-y + {}^1/_2$	$z - {}^1/_2$
V	$x - {}^1/_2$	$-y + {}^1/_2$	$z + {}^1/_2$
VI	$x + {}^1/_2$	$-y + {}^1/_2$	$z + {}^1/_2$
VII	$-x + {}^1/_2$	$y - {}^1/_2$	$-z - {}^1/_2$
VIII	$-x + {}^1/_2$	$y + {}^1/_2$	$-z + {}^1/_2$

In keeping with the above indications of intramolecular strain, it should be noted that the Mo$_1$–Mo$_2$ bond length of 3.267 ± 0.006 Å is some 0.045 Å longer than that for the unstrained linkage of 3.222 Å in [π-C$_5$H$_5$-Mo(CO)$_3$]$_2$[32] and that the azulene ligand is quite badly distorted from planarity, pertinent dihedral angles being C$_1$C$_2$C$_3$C$_{10}$C$_9$–C$_{10}$C$_9$C$_8$C$_4$ = 1° 46′ and C$_{10}$C$_9$C$_8$C$_4$–C$_4$C$_5$C$_6$C$_7$C$_8$ = 18° 46′. Relative to the plane of the π-cyclopentadienyl ring, the π-pentadienyl ligand is bent *away* from the molybdenum atoms by 17° 16′. It is interesting that this distortion is in the opposite sense to that observed in the C$_{10}$H$_8$Fe$_2$(CO)$_5$ molecule,[9,10] presumably (*inter alia*) because of the difference in unstrained iron–iron (~2.7 Å) and molybdenum–molybdenum (~3.2 Å) bond lengths.

All of the remaining bond lengths within the guaiazulene ligand are in keeping with accepted[33] interatomic distances.

The Geometry of the Mo(CO)$_3$ Groups

A careful survey of Tables IV and V shows that the two Mo(CO)$_3$ groups have essentially equivalent stereochemistries, the largest difference between comparable angles being about 7° (O$_1$···Mo$_1$···O$_2$ = 84.5 ± 0.4°, O$_4$···Mo$_2$···O$_5$ = 77.6 ± 0.4°). Since azulene itself is disordered[26] and the two independent Mo(CO)$_3$ groups in the present complex have very similar environments, it is now easy to understand why azulenedimolybdenum hexacarbonyl is able to crystallize in a disordered manner.[13,14]

Average dimensions within the Mo(CO)$_3$ groups are: Mo–C = 1.972 Å, C–O = 1.134 Å. The carbonyl groups *trans* to the molybdenum–molybdenum bond

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[30] The conformation of this ion is surmised from the crystal structure of its reaction product with CH$_3$I–[C$_{10}$H$_8$Mo(CO)$_3$CH$_3$]$_2$.[11,12]

[31] As pointed out by a referee, the asymmetric steric influence of the substituents around the azulene ring could also cause the observed asymmetry of Mo$_2$···C$_4$ *vs.* Mo$_2$···C$_8$ bond distances. We have tended to reject this possibility, mainly on the grounds that there are no abnormally short contacts either to C$_4$ or C$_8$ directly or to the methyl or isopropyl substituents on the azulene ring.

[32] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **37**, 809 (1957).

[33] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1955.

approximate to linearity ($\mathrm{Mo_1{-}C_{17}{-}O_2} = 177.9 \pm 1.7°$, $\mathrm{Mo_2{-}C_{20}{-}O_5} = 179.4 \pm 1.7°$) whereas the remaining four Mo–C–O angles vary from 171.5 ± 1.7 to $176.3 \pm 1.7°$. [Nonlinearity of M–C–O groups is, of course, expected for carbonyl ligands in environments of low symmetry[34] and may also result from the known close *intra*molecular and *inter*molecular contacts.]

Since both π-cyclopentadienyl and π-pentadienyl groups may be regarded as formally tridentate, six-electron donors, the present molecule contains two seven-coordinate molybdenum atoms. The coordination geometry of the metal atoms is related to that in the seven-coordinate species $\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$,[35] $\pi\text{-}C_5H_5Mo(CO)_3C_3F_7$,[36,37] $\pi\text{-}C_5H_5Mo(CO)_3COCF_3$,[38] $[\pi\text{-}C_5H_5Mo(CO)_3]_2$,[32] $\pi\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$,[39] $\pi\text{-}C_5H_5Mo(CO)_3CH_2CO_2H$,[40] $[C_{10}H_8Mo(CO)_3CH_3]_2$,[11,12] $[\pi\text{-}C_5H_5Mo(CO)_2]_2\{P(CH_3)_2\}\{H\}$,[41] and $\pi\text{-}C_5H_5Mo(CO)_3Sn(\pi\text{-}C_5H_5Fe(CO)_2)_2Cl$.[42] A unique feature of the present structure is the large *trans*-Mo–Mo–CO angle of ~160°. In each of the complexes mentioned previously, the corresponding R–Mo–CO or Mo–Mo–CO angle is only ~130°.

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[34] S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).

[35] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

[36] M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 695 (1966).

[37] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

[38] M. R. Churchill and J. P. Fennessey, unpublished work.

[39] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

[40] M. L. H. Green, J. K. P. Ariyante, A. M. Bjerrum, M. Ishaq, and C. K. Prout, *Chem. Commun.*, 430 (1967).

[41] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

[42] J. E. O'Connor and E. R. Corey, *ibid.*, **89**, 3930 (1967).

Contribution from the Department of Chemistry and Lawrence Radiation Laboratory,
University of California, Berkeley, California 94720, and Frick Chemical Laboratory,
Princeton University, Princeton, New Jersey 08540

The Crystal and Molecular Structure of Bis(2,4-pentanedionato)bis(pyridine N-oxide)nickel(II), $Ni(C_5H_7O_2)_2(C_5H_5NO)_2$[1a]

By WILLIAM DeW. HORROCKS, Jr.,[1b] DAVID H. TEMPLETON,[1c,d] and ALLAN ZALKIN[1d]

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The structure of bis(2,4-pentanedionato)bis(pyridine N-oxide)nickel(II), $Ni(C_5H_7O_2)_2(C_5H_5NO)_2$, has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group C2/c, with $a = 14.653 \pm 0.005$ Å, $b = 16.972 \pm 0.005$ Å, $c = 18.344 \pm 0.005$ Å, and $\beta = 100.74 \pm 0.05°$. For $Z = 8$ the measured and calculated densities are 1.32 and 1.324 g/cm,^{3} respectively. Counter data were collected for 2319 independent reflections by the θ–2θ scan technique. The structure was refined, including hydrogens, by least-squares methods to a conventional R value of 0.097. The six oxygen atoms coordinated to the nickel are in nearly regular octahedral disposition with the pyridine N-oxide molecules *cis* to one another and so inclined as to make an average Ni–O–N angle of 121°.

Introduction

Heterocyclic amine N-oxides act as oxygen donor ligands in a variety of transition metal coordination compounds.[2] Very recently structural studies have been reported for compounds which involve pyridine N-oxide acting as a bridging ligand between copper atoms;[3–5] however, no other structural work dealing with complexes of this class of ligand appears to have been done. Not long ago Kluiber and Horrocks[6,7] synthesized and studied complexes of the type bis(2,4-pentanedionato)bis(heterocyclic amine N-oxide)metal(II), hereafter referred to as $M(AA)_2(ligand)_2$, where M = Co, Ni. These complexes belong to the class of neutral donor adducts of $M(AA)_2$ of which the dihydrates,[8,9] $M(AA)_2(H_2O)_2$, and dipyridinates,[10] $M(AA)_2(C_5H_5N)_2$, are known and which involve *trans*-octahedral coordination of the metal in the solid state. On the basis of an analysis of the dipolar (pseudocontact) contribution to the isotropic proton magnetic resonance shifts in solution in the complexes $M(AA)_2(L)_2$ (M = Co or Ni; L = pyridine N-oxide or γ-picoline N-oxide), Kluiber and Horrocks[6] estimated an average M–O–N angle in the range 115–130° for the coordinated heterocyclic amine N-oxides.[11] These results were based on a *trans*-octahedral model for co-

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[2] See, for example, D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966); M. R. Kidd, R. S. Sager, and W. H. Watson, Jr., *ibid.*, **6**, 946 (1967); P. D. Kaplan and M. Orchin, *ibid.*, **6**, 1096 (1967); F. E. Dirkson, E. W. Gowling, and F. F. Bentley, *ibid.*, **6**, 1099 (1967), and references therein.

[3] S. Šćavničar and B. Matković, *Chem. Commun.*, 297 (1967).

[4] R. S. Sager, R. J. Williams, and W. H. Watson, Jr., *Inorg. Chem.*, **6**, 951 (1967).

[5] H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

[6] R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).

[7] R. W. Kluiber and W. D. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

[8] G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

[9] H. Montgomery and E. C. Lingafelter, *ibid.*, **17**, 1481 (1964).

[10] J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965). The complete crystal structure of *trans*-$Co(AA)_2(C_5H_5N)_2$ has recently appeared: R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

[11] A similar estimate was later, but apparently independently, made for the same systems: E. E. Zaev and U. N. Molin, *J. Struct. Chem.* (U.S.S.R.), **7**, 680 (1966).