Contribution from Istituto di Chimica Generale
dell'Università di Milano, Milan, Italy

The Crystal and Molecular Structure of Diiodocarbomethoxycarbonyl(2,2′-bipyridyl)iridium $[IrI_2CO(C_{10}H_8N_2)(C_2H_3O_2)]$[1]

By V. G. ALBANO, P. L. BELLON,[2] and M. SANSONI

Received September 26, 1968

Diiodocarbomethoxycarbonyl(2,2′-bipyridyl)iridium $[IrI_2(COOCH_3)(CO)(C_{10}N_2H_8)]$ crystallizes in space group C_{2h}^5, $P2_1/n$, with unit cell dimensions $a = 8.92$ (1) Å, $b = 17.87$ (2) Å, $c = 10.93$ (1) Å, $\beta = 103.55$ (10)°, and $Z = 4$. The structure has been determined from about 1500 independent reflections (measured by counter methods) and refined by full-matrix least squares to a conventional R factor of 0.043. It consists of a packing of discrete monomeric molecules in which the metal atom displays a distorted octahedral coordination with the two iodine atoms in *trans* positions. On the basis of the observed Ir–C distance (2.05 (2) Å), the carbomethoxy group seems to be linked to the metal *via* a pure σ bond. The observed coplanarity of the –COO group with the metal atom, the carbonyl, and the two nitrogen atoms of bipyridine seems to be due to an angulated hydrogen bond connecting the "ketonic" oxygen of the carbomethoxy group with an α-carbon atom of the bipyridine. The Ir–C bond connecting the metal with the carbonyl ligand is rather short (1.80 (2) Å) although the C–O bond (1.11 (2) Å) and the stretching frequency (2050 cm^{-1}) do not indicate a particularly strong metal–carbonyl interaction. Owing to a steric repulsion of two hydrogen atoms, the 2,2′-bipyridine ligand is not planar, and, consequently, the chelate ring is also not planar.

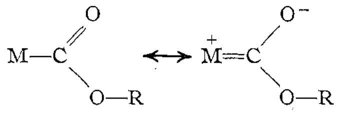
The instabilities of certain metal carbonyl cations in water, which undergo a characteristic reaction to give neutral hydrides and CO_2, support the view that the electrophilic nature of such complexes is localized on the carbon atom of the carbonyl group. The above reaction, in fact, has been shown[3] to occur *via* a carboxylic intermediate M–COOH.

Although no one metal–carboxylic derivative has been found stable enough to be isolated and characterized, Kruck and Noak[4,5] have obtained a number of neutral carboalkoxycarbonyl derivatives of manganese and rhenium, prepared by the nucleophilic attack of alkoxy ions on the corresponding cationic complexes. A similar series of Ir(I) and Rh(I) complexes has been described,[6,7] and, more recently, Malatesta[8] has isolated a series of carboalkoxy derivatives of iridium(III), obtained by the reaction

$$IrI_4(CO)_2^- + 2L + OR^- \longrightarrow IrI_2(COOR)L_2(CO) + 2I^-$$

The present paper deals with the crystal structure determination of one of the iridium(III) compounds, namely, of diiodocarbomethoxycarbonyl(2,2′-bipyridyl)iridium. The interest for this determination arises from the lack of structural information on the carboxy and carboalkoxy groups linked to transition metals.

The electronic interactions between the metal and a carboxy or a carboalkoxy group could be, in principle at least, described in terms of a σ bond plus some contribution of a d_π–p_π interaction of the same kind as that suggested recently by Treichel, *et al.*,[9] for metal–acyl bonds



In this connection it should be noted that the stretching frequency of the carboxylic C═O group in a number of carboalkoxy derivatives[4–6] falls in the range 1620–1700 cm^{-1} (1620 cm^{-1} in this compound) whereas the corresponding range for ordinary esters is 1680–1820 cm^{-1}, with just a narrow overlap with the previous one.

Collection of X-Ray Data and Their Corrections for Systematic Errors

The complex crystallizes from hot 2-propanol into beautiful yellow-orange prismatic tablets. On the basis of Weissenberg and precession photographs, the space group has been determined as monoclinic $P2_1/n$[10] with the following cell dimensions: $a = 8.92$ (1) Å, $b = 17.87$ (2) Å, $c = 10.93$ (1) Å, $\beta = 103.55$ (10)°. Agreement between observed and computed specific gravities has been obtained for $Z = 4$ ($\rho_{calcd} = 2.65$ g/cm^3, $\rho_{measd} = 2.60$ (5) g/cm^3). The latter value was determined by flotation in iodomercurate solution.

The intensities of about 2100 reflections have been measured at room temperature on a Pailred single-crystal diffractometer with Mo Kα radiation monochromatized with a Si [111] single crystal cut.

The crystal was mounted along the a axis to avoid

---

[1] This work was performed under the auspices of the Italian Consiglio Nazionale delle Ricerche.

[2] Address inquiries to this author.

[3] E. L. Muetterties, *Inorg. Chem.*, **4**, 1841 (1965).

[4] T. Kruck and M. Noak, *Chem. Ber.*, **97**, 1693 (1964).

[5] T. Kruck, *Z. Naturforsch.*, **16b**, 709 (1961).

[6] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965).

[7] W. Hieber and F. Frey, *Chem. Ber.*, **99**, 2614 (1966).

[8] L. Malatesta and M. Angoletta, private communication.

[9] P. H. Treichel, R. L. Subkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

[10] This space group refers to a reduced cell. The cell of the *standard* setting having space group $P2_1/c$ is related to the present one in the following way: $a_1 = -a$, $b_1 = b$, $c_1 = a + c$.

systematic double-reflection effects. A set of seven reciprocal lattice layers, from 0*kl* to 6*kl* up to an equi-inclination angle of 16° and to a maximum Υ of 54°, were recorded by the ω-scan technique. After the collection of data had been completed, a number of reflections of the equatorial layer were reevaluated to check whether any crystal decay had occurred. Since no decay was apparent, all of the measured intensities were given the same scale factor throughout the subsequent analysis.

It was then decided that, in order to carry out the structural determination, a 15-fold excess of observations, with respect to the number of parameters (see later) to be determined and refined, would be sufficient. Therefore, 1498 independent reflections, with a relative counting esd lower than 0.25, were sorted out of about 2100 measurements and used in the present analysis.

After the Lorentz and polarization factors had been applied, by taking into account the polarization of the incident beam,[11] the resulting F_o^2 set was corrected for absorption. This effect turned out to be a very important one, owing to the μ value (117 cm^{-1}) and the specimen used. This was a roughly hexagonal platelet with ten well-developed faces, having dimensions 0.028 cm along the rotation axis and 0.015 × 0.018 cm in directions normal to it, the volume being 388×10^{-6} cm.[3]

Very accurate measurements of the faces were taken on an optical-reflection goniometer and the transmission factors—in the range from 0.19 to 0.40—were computed with a program based on the Busing and Levy[12] method.

Structure Solution and Refinement

The coordinates of the iridium and iodine atoms were determined by inspection of a three-dimensional Patterson function and refined isotropically by least squares. The conventional *R* factor for this part of the structure was 0.16. All of the remaining atoms were subsequently located on a difference Fourier. The structure was refined by full-matrix least squares. The variables were three positional and six anisotropical thermal parameters for each of the three heavy atoms, three positional and one isotropic thermal parameters for each of the O, N, and C atoms, and finally an overall scale factor giving a total of 100 parameters.

The atomic scattering factors were chosen as follows: for f_{Ir} and f_{I} the Thomas–Fermi–Dirac statistical model curves[13] corrected for the real part of the anomalous dispersion;[14] for f_{O}, f_{N}, and f_{C} the curves from the self-consistent variational field method.[15]

The minimized function was $\Sigma w(F_o - |F_c|)^2$, *w* being the reciprocal variance of F_o. This variance has been computed from the variance of the corresponding F_o^2, assumed to be[16]

$$V(F_o^2) = V_{cs}(F_o^2) + (AF_o^2)^2$$

where V_{cs} is the counting statistical variance and *A* is a parameter. The assignment of the *A* value was made before refinement, in such a way as to render $w\Delta^2/n$ [with $\Delta^2 = (F_o - F_c)^2$ and *n* being the number of reflections] approximately constant and unitary over the entire range of the F_o's.[17] A preliminary analysis showed that 0.04 was a fairly good value. Before the last two cycles, the evaluation of *A* was repeated and 0.06 was found to be more satisfactory. In both of the weighting schemes, the five strongest reflections (002, 10$\bar{3}$, 061, 160, and 20$\bar{4}$) appeared to be overweighted. The difficulty of assigning them reasonable weights on the basis of the statistical model assumed and, more than that, the possibility of extinction effects led us to disregard these reflections in the refinement. Their values (see Table I), computed on the basis of the final molecular model, appeared to be stronger than the experimental ones, indicating a moderate extinction effect. (The maximum observed discrepancy arises for the lowest angle reflection 002, having $F_o = 450$ and $F_c = 528$ electrons.)

The agreement indices after convergence were $R = \Sigma|F_o - |F_c||/\Sigma F_o = 0.043$ and $R_w = \{\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2\}^{1/2} = 0.055$, with a final value of the error-fit function of 1.30. The above indices, for a preliminary refinement done with the heavy atoms constrained to isotropic vibration, were $R = 0.062$ and $R_w = 0.086$.[18]

None of the 11 hydrogen atoms bonded to the methyl and to the bipyridyl groups has been taken into account in this refinement, nor did any show in a difference Fourier, which was computed on the basis of the final atomic coordinates. In this map the maximum observed electron density was 0.5 e$^-$/Å^3, partly due to vibrational anisotropy in the lighter part of the molecule, which has not been taken into account.

In Table I the final list of computed and observed structure factor moduli is given in electrons. The positional and thermal coordinates for the heavy, anisotropically refined part of the molecule are listed in Table II, and the positional and isotropic thermal parameters for the light part of the molecule are collected in Table III.

The Crystal and Molecular Structure

A layer of the crystal structure composed of molecules related by a set of coplanar inversion centers and

---

(11) W. L. Bond, *Acta Cryst.*, **12**, 375 (1959).

(12) W. R. Busing and H. A. Levy, *ibid.*, **10**, 180 (1957).

(13) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 239 (1957).

(14) "International Critical Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 213.

(15) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

(16) P. A. Agron, R. D. Ellison, and H. A. Levy, *ibid.*, **23**, 1079 (1967).

(17) D. W. J. Cruickshank and D. E. Pilling, "Computing Methods in X-Ray Crystal Analysis," Pergamon Press Ltd., London, 1966.

(18) All of the computations of the present determination have been done on an IBM 7040 computer. The programs used were local versions of the following entries of the 1966 "International World List of Crystallographic Programs"; 7528, 7531, 7532, 7535 for Fourier and Patterson analysis and for structure factors and least-squares computation. Counter data reduction, absorption correction, interatomic distances and angles, and best-plane determinations were based upon Fortran 4 programs prepared in the author's laboratory and were not quoted in the "International World List."

TABLE I

LIST OF COMPUTED (FC) AND OBSERVED (FO) STRUCTURE FACTOR MODULI IN ELECTRONS OBTAINED AFTER CONVERGENCE OF THE LEAST-SQUARES REFINEMENT

H	K	FO	/FC/
L = 0			
0	4	149	144
0	6	166	174
0	8	316	325
0	12	92	96
0	14	181	183
0	16	36	34
0	20	46	48
0	22	73	73
1	4	62	55
1	5	249	249
1	6	446	496
1	7	95	100
1	8	168	169
1	9	52	48
1	12	83	88
1	13	63	62
1	14	164	172
1	16	62	64
1	20	101	100
2	3	121	120
2	4	72	79
2	5	140	142
2	6	71	71
2	7	32	33
2	8	213	229
2	10	100	99
2	11	88	93
2	12	158	164
2	13	73	75
2	14	147	154
2	15	78	74
2	16	34	31
2	18	39	36
2	19	67	70
2	20	55	43
2	22	60	57
3	5	96	95
3	6	214	218
3	7	71	73
3	8	135	140
3	9	209	218
3	10	92	97
3	11	64	63
3	12	29	33
3	13	85	85
3	14	63	64
3	15	44	41
3	16	94	92
3	20	48	49
4	3	166	163
4	4	284	289
4	5	174	171
4	6	38	34
4	7	27	28
4	8	48	49
4	9	57	58
4	10	105	105
4	11	33	32
4	12	120	123
4	13	57	59
4	14	31	34
4	15	68	66
4	17	58	60
4	18	55	55
4	19	55	55
4	22	36	28
5	3	164	164
5	4	24	19
5	6	71	77
5	7	30	31
5	8	71	76
5	9	62	70
5	10	129	136
5	11	139	144
5	16	66	59
6	1	47	44
6	2	39	29
6	3	116	123
6	4	150	160
6	5	105	111
6	9	103	110
6	10	54	57
6	12	57	61
L = 1			
-0	4	58	55
-0	6	344	373
-0	7	128	125
-0	8	143	148
-0	9	59	57
-0	10	54	53
-0	12	68	70
-0	14	177	178
-0	15	39	38
-0	16	40	39
-0	20	107	104
1	3	47	48
-1	3	21	28
1	4	77	81
-1	4	66	73
1	5	201	213
-1	5	106	108
1	6	67	72
-1	6	134	141
-1	7	42	46
1	8	279	283
-1	8	290	303
1	9	46	48
-1	9	27	25
1	11	58	66
-1	11	37	48
1	12	115	121
-1	12	81	87
1	13	100	102
1	14	141	148
-1	14	177	195
1	15	62	60
-1	15	41	45
-1	16	34	35
1	19	49	50
1	20	50	50
-1	20	52	49
1	21	37	37
1	22	60	61
-1	22	63	66
2	1	277	273
-2	3	76	71
2	4	53	50
-2	4	35	32
2	5	155	156
-2	5	145	146
2	6	239	248
-2	6	299	295
2	7	144	148
2	8	177	182
-2	8	128	130
2	9	143	141
-2	9	159	163
2	10	78	77
-2	10	53	57
2	11	78	75
2	12	30	27
-2	12	88	87
2	13	102	102
-2	13	80	79
2	14	119	119
-2	14	153	159
2	15	77	75
2	16	78	78
-2	16	60	58
2	18	48	50
2	20	57	57
-2	20	82	85
3	3	168	160
-3	3	126	131
3	4	199	196
3	5	209	219
-3	5	150	150
3	6	58	54
-3	6	41	37
3	7	49	51
-3	7	78	86
3	8	68	72
-3	8	147	140
3	9	51	49
-3	9	35	32
3	10	93	96
-3	10	58	57
3	11	45	46
-3	11	56	58
3	12	140	143
-3	12	121	124
3	13	74	74
-3	13	36	39
3	14	78	75
-3	14	91	89
3	15	57	55
-3	15	84	85
3	17	59	57
3	19	77	74
-3	19	73	75
3	20	40	40
3	22	43	38
-3	22	49	47
4	1	143	139
4	2	152	150
4	3	144	143
4	4	36	36
-4	5	131	136
4	6	87	90
-4	6	123	136
4	7	39	43
4	8	107	100
-4	8	97	96
4	9	113	116
-4	9	137	145
4	10	107	112
-4	10	121	128
4	11	155	160
-4	11	67	67
-4	12	31	31
4	13	40	40
-4	13	62	60
-4	14	33	24
4	15	49	47
-4	15	31	30
4	16	74	76
-4	16	71	76
4	18	61	59
-4	18	62	58
4	19	36	33
-4	20	36	31
5	2	93	84
5	3	159	145
-5	3	101	107
5	4	191	181
-5	4	242	251
5	5	169	166
-5	5	137	142
-5	6	24	26
-5	8	32	32
5	9	135	136
-5	9	59	61
5	10	59	61
-5	10	108	109
5	12	71	73
-5	12	104	106
-5	15	38	41
6	1	49	43
6	2	55	60
6	3	225	214
-6	3	133	140
6	4	28	22
-6	4	36	37
6	5	57	62
-6	5	32	37
-6	6	26	30
-6	8	36	39
-6	9	38	34
6	10	78	77
-6	10	128	133
6	11	144	148
-6	11	113	119
6	15	44	40
-6	16	49	55
L = 2			
-0	0	450	528
-0	1	69	69
-0	2	32	30
-0	4	73	61
-0	5	103	105
-0	6	75	71
-0	7	83	83
-0	8	225	234
-0	12	78	81
-0	13	104	103
-0	14	164	167
-0	20	43	42
-0	21	52	48
0	22	65	62
1	1	249	258
-1	1	64	62
1	2	88	84
-1	2	156	146
1	3	99	87
1	4	28	26
1	5	78	73
-1	5	67	75
1	6	257	270
-1	6	313	336
1	7	188	185
-1	7	98	96
1	8	171	168
-1	8	119	117
1	9	151	160
-1	9	31	31
-1	10	40	44
1	11	53	60
-1	12	74	74
1	13	43	47
-1	13	37	36
1	14	99	102
-1	14	166	166
1	15	85	83
-1	15	44	49
1	16	66	68
-1	16	36	35
1	20	67	63
-1	20	97	98
2	0	256	243
2	1	36	33
2	2	224	208
2	3	141	134
-2	3	61	59
2	4	112	108
-2	4	28	18
2	5	222	218
-2	5	65	63
2	6	30	24
-2	6	123	124
2	7	78	84
-2	7	42	41
2	8	46	44
-2	8	239	237
2	9	43	45
-2	9	57	59
2	10	82	78
2	11	37	40
-2	11	65	66
2	12	131	126
-2	12	84	84
2	13	117	117
-2	13	33	25
2	14	67	70
-2	14	145	146
2	15	73	71
-2	15	67	69
-2	16	45	42
2	17	54	49
2	19	61	58
-2	19	50	46
2	20	46	40
-2	20	40	36
2	21	54	47
-2	22	54	55
3	1	212	200
3	2	87	84
3	3	151	147
-3	3	70	70
3	4	48	50
-3	4	34	34
3	5	49	45
-3	5	189	194
3	6	113	119
-3	6	196	209
3	7	87	90
3	8	130	133
-3	8	85	92
3	9	128	129
-3	9	171	179
3	10	69	72
-3	10	64	62
3	11	133	135
-3	12	82	79
3	13	43	40
-3	13	98	96
-3	14	96	95
3	15	67	63
3	16	81	83
-3	16	53	54
3	19	58	54
-3	20	74	67
4	2	128	116
4	3	196	183
-4	3	103	112
4	4	161	146
4	5	178	176
-4	5	121	123
4	6	68	63
-4	6	30	31
4	7	34	40
-4	8	85	82
4	9	126	131
-4	9	27	30
4	10	78	81
-4	10	84	89
-4	11	68	68
4	12	85	89
-4	12	105	104
4	13	58	65
-4	14	56	55
-4	15	87	88
-4	16	41	33
4	17	106	103
-4	18	60	61
-4	19	61	61
5	1	54	51
5	2	66	68
5	3	221	215
-5	3	46	43
5	5	72	78
-5	5	83	87
-5	6	84	90
5	7	25	19
5	8	39	40
-5	8	60	59
5	9	52	55
-5	9	107	108
5	10	51	53
-5	10	152	157
5	11	180	183
-5	11	58	58
-5	12	51	51
-5	13	43	46
5	15	43	42
-5	16	77	76
6	1	68	64
6	2	33	19
6	3	126	129
-6	3	80	82
6	4	39	41
-6	4	231	240
6	5	119	120
-6	5	73	74
-6	8	34	31
6	9	121	127
-6	9	61	57
-6	10	96	102
-6	12	88	90
6	13	30	30
-6	16	39	38
L = 3			
-0	1	269	261
-0	2	64	60
-0	4	73	72
0	5	26	23
-0	6	280	277
-0	7	240	248
-0	8	118	119
-0	9	78	78
-0	11	28	28
-0	13	37	35
-0	14	117	118
-0	15	103	108
-0	16	50	50
-0	19	42	42
-0	20	69	64
1	0	251	250
-1	0	472	492
1	1	83	75
-1	1	238	238
1	2	177	169
-1	2	40	23
1	3	112	107
1	4	33	34
-1	4	68	56
1	5	197	189
-1	5	114	124
1	6	31	33
-1	6	109	118
1	7	107	112
-1	7	69	70
1	8	76	80
-1	8	219	220
1	9	83	87
-1	9	71	74
1	10	55	59
1	11	28	29
1	12	101	102
-1	12	61	60
1	13	156	160
-1	13	109	110
1	14	94	96
-1	14	130	134
1	15	47	45
1	19	58	57
1	20	44	41
1	21	67	59
-1	21	56	52
1	22	42	44
2	1	243	230
2	2	86	85
-2	2	169	163
2	3	130	122
-2	3	40	49
-2	5	184	188
2	6	124	123
-2	6	260	264
2	7	164	166
-2	7	139	146
2	8	175	180
-2	8	85	91
2	9	136	139
-2	9	75	73
2	11	114	118
2	12	46	40
-2	12	96	96
2	13	49	46
-2	13	49	51
-2	14	136	139
2	15	86	83
-2	15	57	57
2	16	73	74
2	18	53	46
2	19	41	45
-2	20	91	83
3	0	36	32
-3	0	303	299
3	1	90	92
-3	1	201	187
3	2	180	175
-3	2	28	23
3	3	204	193
-3	3	48	45
3	4	112	118
-3	4	88	87
3	5	225	218
-3	5	57	64
3	6	82	82
-3	6	109	115
3	7	31	30
3	8	26	25
-3	8	220	218
3	9	121	123
-3	9	80	84
3	10	77	76
-3	10	31	33
-3	11	77	77
3	12	98	95
-3	12	78	77
3	13	71	71
-3	13	35	36
-3	14	111	115
-3	15	84	83
3	16	36	34
-3	16	45	44
3	17	85	83
3	19	42	42
-3	19	53	49
-3	22	49	42
4	1	95	83
-4	1	122	124
-4	2	212	210
-4	3	92	98
4	4	28	33
-4	4	47	49
4	5	68	69
-4	5	182	190
-4	6	153	157
4	7	38	42
-4	7	28	31
4	8	61	59
-4	8	60	65
4	9	60	58
-4	9	135	141
4	10	35	35
-4	10	118	122
4	11	179	183
4	12	29	30
-4	12	84	85
-4	13	85	98
-4	14	77	76
4	15	48	47
4	16	37	35
-4	16	57	55
-4	18	42	40
4	19	58	54
-4	19	38	27
-4	20	59	53
-5	0	89	79
5	1	67	62
-5	1	95	93
-5	2	63	46
5	3	161	157
-5	3	45	43
5	4	29	25
-5	4	261	259
5	5	142	147
-5	5	73	74
-5	8	82	82
5	9	150	154
-5	9	49	49
-5	10	94	94
-5	11	57	59
-5	12	104	106
5	13	42	43
-5	14	36	36
-5	15	64	63
-5	16	51	47
6	1	43	43
6	3	179	184
-6	4	32	30
6	5	69	78
-6	5	48	51
-6	6	63	67
6	7	36	39
-6	7	26	19
-6	8	37	42
-6	9	46	50
-6	10	161	167
6	11	140	146
-6	11	39	40
-6	12	59	62
-6	16	77	74
L = 4			
-0	0	258	238
-0	1	175	167
-0	2	118	108
-0	3	75	71
0	4	32	6
-0	5	156	152
-0	6	43	44
-0	7	113	114
-0	8	130	128
-0	9	61	63
-0	11	39	37
-0	12	95	98
-0	13	163	170
-0	14	81	83
-0	19	39	43
-0	20	42	37
-0	21	69	68
1	1	215	208
-1	1	214	208
1	2	60	54
-1	2	116	107
1	3	32	28
-1	3	45	47
1	4	100	100
1	5	28	24
1	6	119	119
-1	6	263	263
1	7	219	208
-1	7	291	294
1	8	125	130
-1	8	95	96
1	9	110	117
1	11	86	85
1	12	55	63
1	13	37	36
1	14	39	39
-1	14	120	125
1	15	108	106
-1	15	91	98
1	16	58	58
1	19	53	58
-1	19	54	42
-1	20	60	61
-2	0	477	492
2	1	83	80
-2	1	256	245
2	2	221	210
-2	2	43	39
2	3	132	127
2	4	54	55
-2	4	39	36
2	5	199	195
-2	5	80	78
2	6	96	96
-2	6	133	131
2	7	55	50
-2	7	91	94
2	8	38	28
-2	8	204	211
2	9	112	110
-2	9	103	104
2	10	56	58
-2	11	30	29
2	12	83	84
-2	12	38	41
2	13	115	116
-2	13	126	129
-2	14	123	123
2	16	38	45
-2	16	35	41
2	17	76	73
2	19	39	37
-2	21	49	49
3	1	118	116
-3	2	189	173
3	3	213	198
-3	3	94	91
3	4	61	60
-3	4	71	66
3	5	76	74
-3	5	227	225
-3	6	744	240
3	7	67	68
-3	7	125	133
3	8	107	104
-3	8	52	52
3	9	71	76
-3	9	80	82
-3	10	51	53
3	11	167	166
-3	11	41	41
3	12	53	54
-3	12	102	105
-3	13	72	77
-3	14	105	106
3	15	39	41
-3	15	63	68
-3	17	32	29
3	18	44	37
3	19	54	49
-3	19	41	50
-3	20	78	74
-4	0	230	213
4	1	66	67
-4	1	188	185
4	2	71	72
-4	2	35	32
4	3	180	166
-4	3	36	32
-4	4	139	140
4	5	163	153
4	6	49	53
-4	6	111	104
-4	8	144	150
4	9	122	121
-4	9	100	102
-4	10	59	61
-4	11	79	80
4	12	35	27
-4	12	80	84
-4	13	43	47
-4	14	78	78
-4	15	80	80
-4	16	62	64
4	17	99	100
-4	18	58	56
-4	19	46	47
-5	1	77	73
5	2	34	30
-5	2	223	201
5	3	180	181
-5	3	75	78
5	4	44	40
-5	4	61	63
5	5	50	53
-5	5	147	147
-5	6	111	119
-5	7	49	46
-5	9	113	118
-5	10	146	149
5	11	155	152
-5	11	35	45
-5	12	82	80
-5	13	60	60
-5	16	57	60
6	0	47	48
-6	0	69	71
-6	1	75	73
6	2	51	47
6	3	80	84
6	4	67	67
-6	4	266	276
6	5	90	92
6	6	33	27
-6	8	68	70
6	9	104	104
-6	10	95	102
-6	11	44	39
6	12	36	35
-6	12	84	85
6	13	34	34
-6	15	50	44
-6	16	39	40
L = 5			
-0	1	255	252
-0	2	35	33
-0	4	78	72
-0	5	39	40
-0	6	146	140
-0	7	257	257
-0	8	102	103
-0	9	71	70
-0	11	63	66
-0	12	47	47
0	13	32	35
-0	14	54	56
-0	15	121	123
-0	16	41	42
-0	19	53	53
1	0	108	101
-1	0	230	225
1	1	114	115
-1	1	258	249
1	2	177	181
-1	2	38	46
1	3	75	74
1	4	42	40
1	5	171	176
-1	5	174	185
1	6	111	110
1	7	69	72
-1	7	104	107
-1	8	138	142
1	9	96	96
-1	9	100	104
1	10	38	34
1	12	79	79
-1	12	58	58
1	13	133	133
-1	13	164	171
-1	14	75	75
1	16	45	44
1	17	54	56
1	19	43	41
1	20	38	33
-1	21	75	76
2	1	100	102
-2	1	184	177
-2	2	129	125
2	3	143	135
-2	3	78	73
2	4	67	67
2	5	34	33
-2	5	102	104
2	6	51	48
-2	6	170	169
2	7	95	97
-2	7	269	268
2	8	108	108
-2	8	50	53
2	9	46	50
-2	10	38	37
2	11	145	141
2	12	78	74
-2	12	62	60
-2	14	94	93
2	15	71	70
-2	15	106	108
2	16	42	42
2	19	54	55
-2	19	48	49
-2	20	64	56
-3	0	268	260
3	1	52	51
-3	1	215	212
3	2	111	110
-3	2	65	59
3	3	146	139
3	5	138	138
3	6	60	60
-3	6	141	141
-3	7	88	88
3	8	66	67
-3	8	156	163
3	9	123	123
-3	9	109	112
-3	11	44	47
3	12	34	37
3	13	47	45
-3	13	115	119
-3	14	91	89
-3	15	54	59
-3	16	41	45
3	17	88	87
-3	21	52	49
4	1	42	44
-4	1	52	44
4	2	51	48
-4	2	114	114
4	3	193	195
-4	3	110	106
-4	4	41	47
4	5	76	80
-4	5	165	173
-4	6	126	133
-4	7	116	116
4	9	31	28
-4	9	95	100
4	10	40	36
-4	10	82	83
4	11	134	138
-4	11	53	55
4	12	48	43
-4	12	104	106
-4	13	60	59
-4	14	80	83
-4	15	58	61
4	19	43	43
-4	19	53	52
-4	20	50	54
-5	0	120	118
-5	1	159	152
5	2	44	39
-5	2	50	41
5	3	103	101
5	4	66	60
-5	4	191	175
5	5	83	88
-5	6	50	57
-5	8	106	111
5	9	94	95
-5	9	102	104
5	10	40	44
-5	10	42	43
-5	11	58	56
-5	12	61	65
-5	13	47	42
-5	15	61	60
6	2	54	59
-6	2	186	175
6	3	79	84
-6	3	99	96
-6	4	50	50
-6	5	110	118
-6	6	64	65
-6	7	40	41
6	8	38	37
6	9	37	31
-6	9	51	48
6	10	36	40
-6	10	128	132
6	11	80	84
-6	12	65	64
-6	13	33	37
L = 6			
-0	0	42	41
-0	1	171	175
-0	2	147	142
-0	3	71	69
-0	5	150	151
-0	6	89	91
-0	7	93	94
-0	9	98	97
-0	12	42	45
-0	13	160	159
-0	16	42	45
0	17	36	32
0	19	35	29
1	1	132	134
-1	1	222	218
1	2	50	48
1	3	119	120
1	4	95	91
-1	4	38	39
1	5	53	51
-1	5	45	50
-1	6	86	87
1	7	161	170
-1	7	281	278
1	8	93	93
-1	8	71	74
1	9	47	48
-1	9	49	50
1	10	47	43
-1	10	36	32
1	11	109	108
1	12	86	89
1	15	90	85
-1	15	118	116
1	16	35	35
1	19	67	60
-1	19	52	50
2	0	70	60
-2	0	184	181
2	1	89	91
-2	1	222	226
2	2	146	142
2	3	125	120
-2	4	47	44
2	5	142	137
-2	5	106	110
2	6	93	95
-2	6	65	63
-2	7	111	109
2	8	74	73
-2	8	77	76
2	9	133	127
-2	9	86	82
2	13	87	83
-2	13	161	157
-2	14	67	67
2	16	56	54
2	17	79	78
3	1	40	40
-3	1	93	89
3	2	73	70
-3	2	60	64
3	3	186	185
3	4	47	50
-3	4	51	50
3	5	79	79
-3	5	133	129
3	6	35	32
-3	6	91	99
3	7	38	33
-3	7	202	201
3	8	41	42
3	10	52	54
3	11	139	139
3	12	59	60
-3	12	76	72
-3	14	67	66
-3	15	100	101
3	19	43	47
-3	19	54	55
-3	20	47	49
4	0	45	50
-4	0	123	134
4	1	49	45
-4	1	171	171
-4	2	101	96
4	3	113	113
4	4	84	85
-4	4	35	36
4	5	99	97
-4	5	39	34
-4	6	93	93
-4	7	54	54
4	8	45	44
-4	8	135	129
4	9	94	93
-4	9	107	107
4	10	50	47
-4	11	48	52
-4	13	89	93
-4	14	57	57
-4	15	51	51
4	16	35	30
-4	16	42	46
4	17	80	76
5	2	78	80
-5	2	120	116
5	3	106	106
-5	3	128	120
-5	4	62	56
5	5	37	32
-5	5	140	145
5	6	46	51
-5	6	60	62
-5	7	72	72
5	9	36	37
-5	9	72	74
5	10	57	67
-5	10	78	78
5	11	97	94
-5	11	55	57
-5	12	78	79
-5	13	63	65
-5	15	44	41
6	0	53	48
-6	0	38	38
-6	1	85	87
6	3	49	49
6	4	81	88
-6	4	148	153
6	5	64	61
-6	6	53	52
6	8	39	34
-6	8	43	44
6	9	57	49
-6	9	68	72
6	10	45	53
-6	10	60	56
-6	11	55	56
-6	15	52	44
L = 7			
-0	1	159	158
-0	2	39	45
-0	3	84	82
-0	4	55	54
-0	5	59	56
-0	7	193	193
-0	8	78	80
-0	10	50	56
-0	11	67	64
-0	12	73	78
-0	15	94	89
-0	19	52	51
1	0	65	63
-1	0	37	36
1	1	124	124
-1	1	179	183
1	2	125	126
-1	2	85	85
1	3	75	76
1	4	46	50
-1	4	36	39
1	5	129	130
-1	5	123	125
1	6	108	112
-1	6	39	41
-1	7	102	109
1	8	80	79
1	9	104	105
-1	9	86	90
1	13	89	89
-1	13	155	156
1	16	61	64
1	17	57	53
2	1	47	47
-2	1	183	182
2	2	107	104
2	3	146	142
2	4	64	62
2	5	92	88
-2	5	72	68
2	6	41	37
-2	6	39	46
2	7	58	60
-2	7	257	256
2	8	42	42
2	10	64	70
2	11	121	125
2	12	81	81
2	14	34	31
2	15	45	40
-2	15	119	113
-2	19	52	48
3	0	49	52
-3	0	103	109
3	1	63	56
-3	1	215	210
3	2	42	39
-3	2	62	62
3	3	102	99
3	4	108	107
3	5	96	95
-3	5	100	98
3	6	48	46
-3	6	72	72
-3	7	90	87
3	8	69	76
-3	8	69	72
3	9	88	92
-3	9	99	93
-3	13	138	134
-3	14	44	35
-3	15	37	25
3	16	46	40
3	17	77	72
3	19	42	40
-4	1	79	74
4	2	98	102
-4	2	52	53
4	3	112	117
-4	3	85	81
4	4	36	33
-4	4	49	54
4	5	40	45
-4	5	123	121
4	6	40	44
-4	6	47	54
-4	7	163	166
-4	9	35	39
4	10	70	75
4	11	97	94
-4	11	48	51
4	12	35	36
-4	12	79	76
-4	13	38	41
-4	14	38	38
-4	15	80	77
-4	19	46	46
5	0	41	42
-5	0	80	80
-5	1	155	148
-5	2	83	83
5	3	66	59
5	4	107	108
-5	4	56	54
5	5	61	57
-5	5	53	51
-5	6	96	88
5	8	44	45
-5	8	69	73
5	9	54	49
-5	9	99	101
-5	11	56	46
-5	13	67	68
6	2	99	80
-6	2	98	100
6	3	38	33
-6	3	109	113
-6	4	57	58
-6	5	113	119
6	6	56	56
-6	7	55	55
6	8	41	40
-6	10	76	76
-6	11	76	76
-6	12	71	68
L = 8			
-0	0	62	69
-0	1	125	124
-0	2	116	124
-0	4	52	50
-0	5	87	87
-0	6	83	84
0	7	39	37
-0	8	83	84
-0	9	79	81
-0	13	95	96
-0	16	53	54
0	17	35	32
0	18	37	32
1	1	55	52
-1	1	110	109
1	2	97	98
-1	2	45	41
1	3	115	113
1	4	73	70
-1	4	55	59
1	5	82	78
-1	5	61	57
1	6	39	42
1	7	78	79
-1	7	179	187
1	8	48	51
1	10	62	64
-1	10	47	50
1	11	78	76
1	12	78	78
-1	12	64	69
1	15	40	39
-1	15	93	91
2	0	70	64
2	1	61	62
-2	1	175	172
2	2	63	61
2	3	80	76
2	4	96	95
-2	4	42	42
2	5	69	69
-2	5	77	74
2	6	66	70
-2	6	49	42
-2	7	100	96
2	8	66	68
2	9	90	77
-2	9	68	63
-2	13	142	133
2	16	48	49
2	17	50	51
3	1	143	138
3	2	100	100
3	3	101	99
-3	3	55	44
3	4	55	49
3	5	47	49
-3	5	65	64
3	6	42	46
-3	7	217	216
3	10	78	81
3	11	82	82
3	12	49	52
-3	15	90	88
-3	19	43	42
4	0	38	44
-4	0	70	61
-4	1	166	164
-4	2	76	78
4	3	46	50
4	4	119	117
4	5	51	45
-4	5	78	74
-4	6	77	76
-4	7	67	61
4	8	45	48
-4	8	39	41
4	9	44	43
-4	9	91	97
4	10	52	56
4	12	40	45
-4	13	120	115
-5	1	41	40
5	2	77	84
-5	2	51	44
-5	3	87	89
-5	4	50	43
-5	5	112	112
5	6	58	53
-5	7	111	117
-5	8	47	51
-5	11	69	69
-5	12	61	57
6	0	44	57
-6	1	125	111
-6	2	72	72
-6	3	53	55
6	4	98	79
-6	4	58	57
-6	5	48	56
-6	6	44	46
-6	8	50	46
-6	9	93	93
-6	11	54	41
-6	13	58	53
L = 9			
-0	2	69	74
-0	3	39	40
-0	4	46	45
-0	5	52	50
-0	6	38	34
-0	7	82	84
-0	8	40	37
-0	10	52	57
-0	11	47	49
-0	12	72	79
-0	15	45	46
1	0	64	64
1	1	57	59
-1	1	106	108
1	2	73	72
-1	2	61	65
1	4	78	90
1	5	45	41
-1	5	54	57
1	6	57	58
-1	6	81	86
-1	7	60	63
1	8	79	82
-1	8	58	67
1	9	50	54
-1	9	59	55
-1	13	98	89
1	16	52	49
-2	1	138	137
2	2	99	102
-2	2	50	51
2	3	79	94
2	4	44	43
2	5	54	55
-2	5	61	67
-2	7	159	165
2	10	77	80
2	11	47	51
2	12	57	57
-2	15	77	78
-3	1	163	157
3	3	41	39
3	4	114	109
-3	4	49	51
3	5	35	28
-3	5	87	91
3	6	35	32
-3	7	78	77
3	8	40	45
-3	9	59	63
3	10	47	50
-3	13	106	110
-4	1	93	96
4	2	80	81
-4	4	40	31
-4	5	52	55
-4	7	164	166
4	10	65	69
-4	11	45	42
-4	15	84	82
-5	1	109	114
-5	2	91	86
-5	3	39	29
-5	5	62	66
-5	6	62	56
-5	7	54	54
-5	8	42	35
-5	9	83	84
-6	1	45	45
-6	3	121	102
-6	5	89	89
-6	7	82	72
-6	8	55	45
-6	10	40	31
-6	11	79	72
L = 10			
-0	0	83	85
-0	1	64	66
-0	2	53	57
-0	4	75	72
-0	6	74	73
-0	8	67	72
-0	9	58	54
-0	13	48	44
0	14	41	34
-1	1	50	48
1	2	90	93
-1	2	80	80
1	3	53	53
-1	3	44	40
1	4	38	40
-1	4	57	52
1	5	46	50
-1	5	56	56
1	6	49	52
-1	6	64	64
-1	7	94	103
1	10	70	74
-1	10	49	55
1	11	41	37
1	12	65	61
-1	12	69	70
-1	14	43	41
-1	15	43	45
2	0	56	47
-2	0	100	98
-2	1	122	123
-2	2	39	31
2	4	107	110
-2	4	60	59
-2	5	48	46
-2	6	51	52
-2	7	50	55
2	8	54	53
-2	8	87	77
-2	9	46	47
-2	13	78	84
-3	1	89	94
3	2	85	86
-3	2	68	70
3	6	38	38
-3	6	61	62
-3	7	151	159
3	10	71	72
-3	15	68	71
4	0	39	32
-4	1	113	120
-4	2	58	54
4	4	89	87
-4	4	44	43
-4	5	67	71
-4	7	49	48
4	8	37	34
-4	9	66	66
-4	13	98	96
-5	1	76	73
-5	3	46	55
-5	5	58	56
-5	7	119	116
-5	8	58	56
-6	1	107	88
-6	2	63	74
-6	3	48	49
-6	5	73	67
-6	9	78	75
L = 11			
-0	2	99	99
0	4	47	43
-0	5	49	47
-0	6	63	63
-0	10	59	64
-0	12	56	63
1	0	56	60
-1	0	104	102
-1	1	63	67
-1	2	41	38
1	4	99	101
-1	4	69	69
1	6	40	41
-1	6	57	67
1	8	58	59
-1	8	79	84
-2	1	41	48
2	2	85	87
-2	2	71	77
2	4	38	29
-2	5	41	44
2	6	42	41
-2	6	80	81
-2	7	78	87
2	10	68	71
-2	10	51	44
-2	12	54	53
-3	0	109	106
-3	1	87	87
3	4	91	90
-3	4	51	52
-3	5	39	39
-3	7	45	47
3	8	43	38
-3	8	57	61
-3	9	39	39
3	10	42	40
-3	13	70	72
-3	14	43	36
-4	1	77	77
4	2	57	60
-4	2	56	54
-4	6	68	69
-4	7	115	114
-4	8	41	42
-4	15	52	57
-5	0	50	49
-5	1	81	80
-5	2	64	56
-5	5	56	59
-6	6	42	41
L = 12			
-0	0	62	63
-0	4	80	80
-0	8	57	58
1	2	76	80
-1	2	77	75
1	6	42	42
-1	6	56	63
-1	10	53	51
-2	0	88	97
-2	1	65	57
2	4	72	83
-2	4	50	49
-2	8	73	71
-3	1	43	36
3	2	49	56
-3	2	59	62
-3	6	73	75
-3	7	65	73
-4	0	94	86
-4	1	67	62
4	4	45	51
-4	5	40	29
-4	7	40	32
-4	8	49	48
-4	13	52	52
L = 13			
-0	2	62	65
-1	0	51	65
1	4	69	75
-1	4	43	56
-2	2	56	59
-2	6	59	59
-3	0	78	83
-3	1	49	36
-3	8	50	61
-4	2	44	51
-4	6	58	68
-4	7	51	51
L = 14			
-2	0	64	65
-3	2	45	47
-4	0	86	85

screw axes is shown in Figure 1. The crystal consists of a packing of discrete monomeric molecules related by the space group symmetry operators. An examination of the intermolecular contacts shows as an essential feature of this packing the piling up, at the usual van der Waals distances, of bipyridine and carbomethoxy groups around the inversion centers in a characteristic sequence . . . dipy–$COOCH_3$–$COOCH_3$–dipy. . . (see Figure 1). The metal atoms lie near the screw axes and so do the iodine atoms which pack together at distances of 3.86 and 3.97 Å, giving a van der Waals radius of iodine well below the value of 2.15 Å predicted by Pauling.[19]

An isolated molecule is shown perspectively in

---

[19] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

TABLE II[a-d]

POSITIONAL AND THERMAL ANISOTROPIC PARAMETERS OF THE IRIDIUM ANDIODINE ATOMS

Atom	x/a	y/b	z/c	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Ir	2745 (1)	1341 (0)	2910 (1)	80 (1)	−0 (0)	39 (1)	22 (0)	−2 (0)	52 (0)
I(1)	1921 (2)	2780 (1)	2600 (1)	177 (2)	29 (1)	103 (2)	26 (0)	14 (1)	88 (1)
I(2)	3553 (2)	−108 (1)	3077 (1)	144 (2)	11 (1)	84 (2)	24 (0)	0 (1)	105 (11)

[a] All values $\times 10^{-4}$. [b] The β_{ij} terms are the coefficients of the atomic thermal ellipsoids in the form: $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{ij}$. [c] No significant deviations in the atomic positional coordinates are noticeable when the heavy atoms are refined with isotropic thermal coefficients. These isotropic coefficients are 2.55, 3.92, and 3.86 Å^2 for Ir, I(1), and I(2), respectively. [d] The numbers in parentheses here and in the succeeding tables are the esd's in the last significant digits.

TABLE III[a,b]

POSITIONAL AND THERMAL ISOTROPIC PARAMETERS OF THE C, O, AND N ATOMS

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	4690 (23)	1627 (10)	3607 (17)	4.0 (3)	C(13)	−2545 (29)	403 (11)	1689 (23)	6.1 (5)
C(1)	5894 (16)	1798 (8)	4052 (13)	5.3 (3)	C(14)	−1689 (29)	543 (11)	785 (23)	6.1 (5)
C(2)	3302 (21)	1406 (8)	1195 (14)	3.0 (3)	C(15)	−222 (27)	838 (11)	1083 (20)	5.3 (3)
C(2)	2501 (19)	1245 (8)	211 (14)	6.1 (3)	N(2)	1962 (19)	1290 (6)	4626 (13)	3.7 (3)
C(3)	4666 (16)	1656 (6)	1272 (13)	5.0 (3)	C(21)	498 (23)	1094 (8)	4475 (16)	3.6 (3)
C(3)	5138 (26)	1829 (10)	95 (20)	5.1 (3)	C(22)	−213 (27)	1068 (11)	5570 (21)	5.2 (5)
N(1)	408 (19)	994 (6)	2307 (13)	3.7 (3)	C(23)	721 (29)	1298 (11)	6699 (21)	5.9 (5)
C(11)	−321 (21)	875 (8)	3242 (16)	3.3 (3)	C(24)	2161 (26)	1499 (10)	6770 (20)	5.1 (3)
C(12)	−1823 (22)	589 (10)	2934 (17)	4.1 (3)	C(25)	2851 (25)	1489 (10)	5785 (19)	4.5 (3)

[a] All values $\times 10^{-4}$. [b] The atoms are labeled according to Figure 2.

Figure 2 where the key lettering to Tables II–IV is given.

The coordination around the central iridium is a rather distorted octahedral one, the distortion resulting from stereochemical as well as packing effects. The iodine atoms occupy two *trans* positions at distances of 2.672 (2) and 2.684 (2) Å from iridium. The I(1)–Ir–I(2) angle, 176.7° (1°), seems to be distorted from the ideal value of 180° as a consequence of the short intermolecular contacts separating the halogen atoms. The remaining corners of the octahedron are occupied by two nitrogen and two carbon atoms. This part of the molecule (Ir, N(1), N(2), C(1), and C(2)) is planar within one or two esd's of each of the five atoms (in monoclinic coordinates the "best plane"[20] through these atoms has the equation: $(-2.421x + 17.107y - 0.359z - 1.540 = 0.0)$. The deviations from planarity for all of the atoms excluding the two halogens are shown in Figure 3.

The two iridium–carbon distances are quite different as expected. The longer, 2.05 Å, connects the metal with the sp^2-hybridized carbon of the carbomethoxy group. The presence of a purely covalent σ Ir–I bond offers the opportunity to use the covalent radius of Ir *in this compound* to assess the character of the metal–carbomethoxy interaction. The iodine covalent radius being 1.33 Å, a value of r_{Ir} = 1.35 Å results and the predicted value for a σ bond between the metal and an sp^2-hybridized carbon (r_{C} = 0.74 Å) is 2.09 Å. The observed Ir–C distance of 2.05 (2) Å is shorter by two esd's so that there is scarce, if any, evidence of d_π–p_π interaction. Moreover, a number of Pt–CH_3 bonds with the metal atom in various oxidation states[21-23] are 2.05 Å long. This distance is not

TABLE IV

SELECTED INTERATOMIC DISTANCES AND ANGLES WITHIN A SINGLE MOLECULAR UNIT OF $IrI_2(CO)(C_{10}N_2H_8)(C_2H_3O_2)$

Atoms	Distances, Å	Atoms	Angles, deg
(i) Bond Distances and Angles around the Iridium Atom			
Ir–I(1)	2.672 (2)	I(1)–Ir–I(2)	176.7 (0.1)
Ir–I(2)	2.684 (2)	I(1)–Ir–C(1)	89.4 (0.6)
Ir–C(1)	1.80 (2)	I(1)–Ir–C(2)	87.0 (0.4)
Ir–O(1)	2.91 (1)	I(1)–Ir–N(1)	91.2 (0.3)
Ir–C(2)	2.05 (2)	I(1)–Ir–N(2)	90.9 (0.3)
Ir–N(1)	2.13 (2)	I(2)–Ir–C(1)	91.6 (0.6)
Ir–N(2)	2.15 (2)	I(2)–Ir–C(2)	89.9 (0.4)
		I(2)–Ir–N(1)	88.2 (0.3)
		I(2)–Ir–N(2)	92.0 (0.3)
		C(1)–Ir–N(1)	173.2 (0.8)
		C(1)–Ir–N(2)	96.9 (0.8)
		C(1)–Ir–C(2)	87.5 (0.8)
		C(2)–Ir–N(2)	175.2 (0.6)
(ii) Bond Distances and Angles within the Carbonyl and Carbomethoxy Groups			
C(1)–O(1)	1.11 (2)	Ir–C(2)–O(2)	126.6 (1.6)
C(2)–O(2)	1.18 (2)	Ir–C(2)–O(3)	112.8 (1.1)
C(2)–O(3)	1.28 (2)	O(2)–C(2)–C(3)	120.6 (1.9)
C(3)–O(3)	1.48 (3)	C(2)–O(3)–C(3)	118.3 (1.4)
(iii) Bond Distances and Angles within the 2,2′-Bipyridine and the Chelate Ring			
N(1)–C(11)	1.35 (3)	Ir–N(1)–C(11)	115.0 (1.1)
N(1)–C(15)	1.36 (3)	Ir–N(1)–C(15)	121.2 (1.5)
N(2)–C(21)	1.33 (3)	Ir–N(2)–C(21)	114.4 (1.2)
N(2)–C(25)	1.38 (2)	Ir–N(2)–C(25)	123.9 (1.4)
C(11)–C(12)	1.40 (3)	N(1)–C(11)–C(21)	116.0 (1.7)
C(12)–C(13)	1.40 (3)	N(2)–C(21)–C(11)	117.5 (1.9)
C(13)–C(14)	1.40 (4)	C(11)–N(1)–C(15)	123.5 (1.7)
C(14)–C(15)	1.38 (3)	C(21)–N(2)–C(25)	121.5 (1.8)
C(21)–C(22)	1.40 (3)	C(11)–C(21)–C(24)	177.5 (1.7)
C(22)–C(23)	1.38 (3)	C(14)–C(11)–C(21)	174.2 (1.5)
C(23)–C(24)	1.38 (4)		
C(24)–C(25)	1.36 (3)		
C(11)–C(21)	1.43 (2)		

---

(20) W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).

(21) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.* (London), **A266**, 527 (1962).

(22) J. E. Lyndon and M. R. Truter, *J. Chem. Soc.*, 6899 (1965).

(23) N. A. Bayley, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russel, *Chem. Commun.*, 396 (1966).

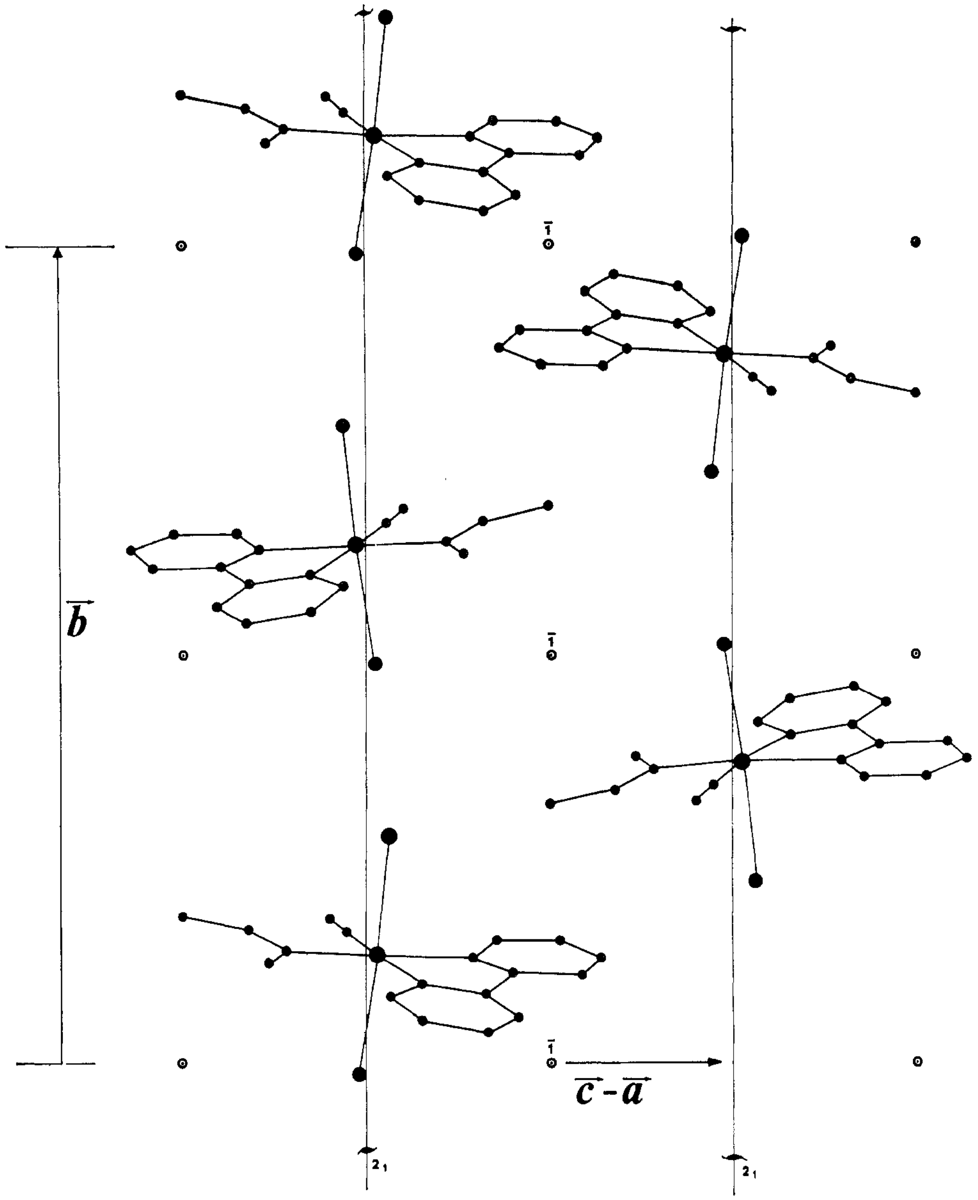


Figure 1.—Packing of molecules related by inversion centers ($\bar{1}$) and screw axes (2_1).

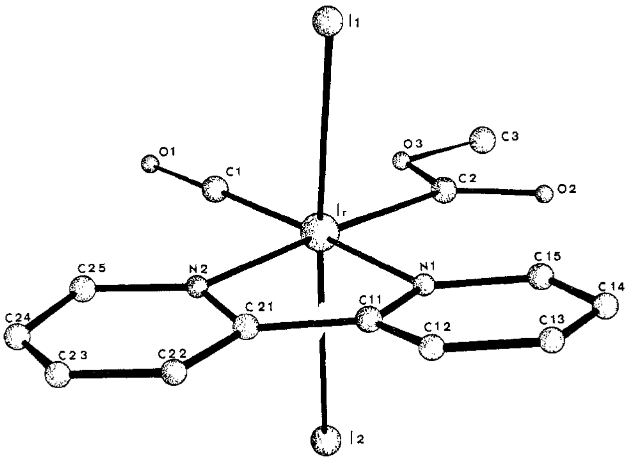


Figure 2.—A perspective view of IrI$_2$(CO)(C$_{10}$N$_2$O$_8$)(C$_2$H$_3$O$_2$).

strictly comparable to the present one, because of the different hybridization character of the carbon, but it may be assumed that—within a range of one or two esd's—the atomic contraction in going from Ir to Pt is offset by the increment of the carbon radius in going from an sp^2 to an sp^3 hybridization state. Still an independent indication of a possible d$_\pi$–p$_\pi$ interaction arises from the coplanarity of the ketonic CO in the carbomethoxy group with the square of ligands represented in Figure 3. In fact, if the –COO group is bonded to the metal *via* a σ bond, it should be expected to rotate around the junction. There is however an indication that the –COO could be constrained into the plane of Ir, N(1), N(2), C(1), and C(2) by an angulated hydrogen bond connecting O(2) and the carbon atom C(15) of the bipyridine (see later).

The carbonyl group is linearly bonded to the metal atom, the Ir–C–O angle being 179 (2°). The distance

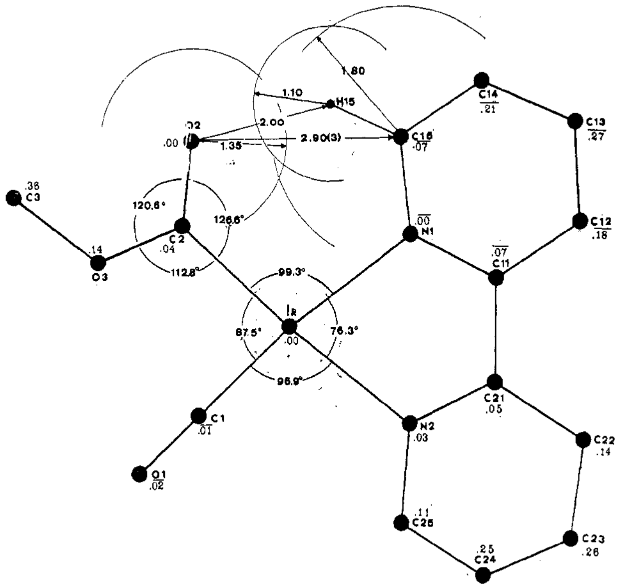


Figure 3.—A projection of the molecule on the "best" plane passing through Ir, N(1), N(2), C(1), and C(2) atoms (the iodine atoms are not shown). (The decimal numbers near the key letters represent the distances of each atom from the best plane.)

of 1.80 (2) Å from metal to carbon falls among the shortest third transition metal–carbonyl interactions reported in the literature for neutral carbonyls.[24] This distance however should not be taken as an indication of a particularly strong metal–carbonyl interaction, which should be accompanied by a longer C–O distance (the observed value is 1.11 (3) Å) and a lower carbonylic stretching frequency (observed frequency is 2050 cm^{-1}).

The iridium–nitrogen bond lengths, 2.13 (2) and 2.15 (2) Å, are strictly comparable. There is also good agreement between the metal–nitrogen bonds in this determination and in a number of structural investigations on species containing platinum bonded to pyridic nitrogen.[21–23] A relevant deformation of the ideal octahedral coordination around the metal is due to the presence of the chelate ring. The N(1)–Ir–N(2) angle of about 76° is the same as in trimethylacetylacetonyl(2,2′-bipyridyl)platinum.[21]

The 2,2′-Bipyridine and the Carbomethoxy Ligands

The 2,2′-bipyridine configuration does not show relevant differences with respect to the free molecule, apart from the obvious fact that here the molecule is constrained into the *cis* form, while the crystal structure of bipyridine displays the *trans* conformation.[25] The two rings are rotated around their junction C(11)–C(21) by 7.5°, in agreement with previous results.[21] This rotation comes from a repulsive interaction of the hydrogen atoms bonded to C(12) and C(22); these hydrogens, when placed in postulated positions at 1.08 Å from the appropriate carbon atoms in directions bisecting the angles C(11)–C(12)–C(13) and C(21)–C(22)–C(23), are separated by 2.2 Å. Owing to the relative rotation of one pyridic ring with respect to the other, the chelate ring is not planar, the distortion being such that the two carbon atoms of the junction lie 0.05 and 0.07 Å, respectively, above and below the "best" plane defined by Ir and the metal-bonded N and C atoms.

The two rings are planar well within the esd's of each single atom[26] and the C–N and C–C distances listed in Table IV agree with previous results.[21,25]

Distances and angles within the carbomethoxy group have been compared with those found in a recent statistical examination carried out on carboxylic acids and esters.[27] The "ketonic' C(2)–O(2) distance of 1.18 (2) Å compares well with the statistical mean value of 1.223 (4) Å. The C(2)–O(3) bond of 1.28 (2) Å similarly compares with the statistical one of 1.302 (6) Å.

A relevant distortion is apparent in the bond angles around the sp^2-hybridized carbon C(2). The O(2)–C(2)–O(3) angle is 120.6° whereas the statistics indicate 124° as the most probable value and a large difference is found among the two adjacent angles Ir–C(2)–O(2) and Ir–C(2)–O(3) (see Figure 3). This deformation is certainly due to the short distance (2.90 (2) Å) separating the atoms O(2) and C(15). In Figure 3 the van der Waals radii for O(2), C(15), and H(15) (the last in its "postulated" position) are given. The values reported are well-checked data[28] and the possibility arises of the presence of an angulated hydrogen bond O(2)–H(15)–C(15) which makes the distances O(2)–C(15) (2.90 Å) and O(2)–H(15) (2.0 Å) much shorter than in the predicted van der Waals interactions (3.15 and 2.45 Å, respectively). The well-known reactivity of the α position in pyridic rings, as well as charge-distribution analyses in pyridine and in similar aromatic systems,[29] supports the view that a fractional positive charge—a condition for hydrogen bonding—is associated with the α-bonded hydrogen. This effect and possibly only a limited Ir–C d_π–p_π interaction seem to be responsible of the observed coplanarity of the –COO system with the metal and the metal-bonded C and N atoms.

Acknowledgments.—The authors wish to thank the Italian Consiglio Nazionale delle Ricerche for financial support and Professor V. Scatturin for his continuous interest. The courtesy of Dr. M. Angoletta, who has prepared the crystals, is also acknowledged.

---

[24] F. Calderazzo, "Organic Syntheses *via* Metal Carbonyls," Vol. 1, Interscience Publishers Ltd., London, 1967.

[25] L. L. Merritt and E. D. Schroeder, *Acta Cryst.*, **9**, 801 (1965).

[26] The best planes through the pyridic rings are $3.166x + 16.548y - 3.644z - 1.406 = 0$ for ring 1 and $2.226x + 16.979y - 3.587z - 1.125 = 0$ for ring 2, in monoclinic coordinates.

[27] A. Mugnoli, unpublished results.

[28] A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961. The van der Waals radius of hydrogen is usually assumed to be in the range 1.1–1.3 Å. The present considerations are based upon the lower limit.

[29] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).