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Structural Studies of Organonitrogen Compounds of the Transition Elements. IV. The Crystal and Molecular Structure of Benzo[*c*]cinnolinebis(tricarbonyliron), $C_{12}H_8N_2Fe_2(CO)_6$[1]

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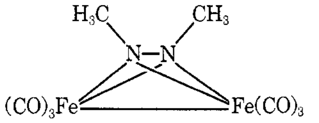
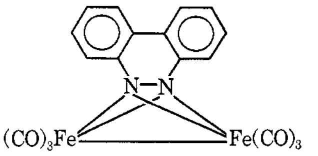
A crystallographic determination of the structure of benzo[*c*]cinnolinebis(tricarbonyliron) has been carried out. Crystals of this material are triclinic, with two formula units in a primitive cell of dimensions a = 7.892 (12) Å, b = 9.037 (14) Å, c = 14.884 (24) Å, α = 86° 32′ (2′), β = 113° 39′ (2′), and γ = 107° 0′ (2′). The probable space group is C_i^1-P$\bar{1}$; observed and calculated densities are 1.64 (2) and 1.645 g/cm³, respectively. A full-matrix least-squares refinement based upon 1970 independent counter data converged to a conventional R factor of 6.0%. The monomeric, binuclear $C_{12}H_8N_2Fe_2(CO)_6$ molecule contains two $Fe(CO)_3$ groups linked by two Fe–N–Fe bridges through the nitrogen atoms of the benzo[*c*]cinnoline molecule and also by an iron–iron bond of length 2.508 (4) Å. The benzo[*c*]cinnoline ligand is significantly nonplanar, and the overall molecular symmetry is approximately C_s-m. The N–N bond length is 1.399 (8) Å and the mean Fe–N distance is 1.914 (3) Å.

Introduction

The previous paper in this series[2] reported the results of a crystallographic determination of the structure of the azomethane iron carbonyl complex $[CH_3NFe(CO)_3]_2$. A structure (I) in agreement with a previous proposal[3] was obtained for this compound, thus providing the first confirmed example of a nitrogen-bridged binuclear metal carbonyl derivative in which a N–N bond links the two bridging nitrogen atoms. Though the configuration I was not unanticipated, certain details of the structure (in particular the Fe–Fe and Fe–N bond lengths) showed surprising variations from those observed in other closely related N-bridged binuclear compounds.[4-9] It was of interest to establish whether these variations were a direct consequence of the presence of a N–N bond in $[CH_3NFe(CO)_3]_2$, and hence a structural investigation of benzo[*c*]cinnolinebis(tricarbonyliron), proposed[10] to have a configuration (II) in which the methyl groups of I are replaced by the fused benzo[*c*]cinnoline ring system, was undertaken.



I



II

The title compound was first reported by Bennett,[10] who prepared it in high yield from the reaction of benzo[*c*]cinnoline with iron pentacarbonyl and proposed structure II. It has also been obtained by Campbell and Rees[11] as a minor product (5% yield) of the reaction of 2,2′-diazidobiphenyl with diiron enneacarbonyl. They also assigned structure II to this product, and supported this assignment by demonstrating that benzo[*c*]cinnoline was obtained from oxidation of the complex with ferric chloride. The results of a complete structural determination of II are reported herein.

Collection and Reduction of the Intensity Data

A sample of $C_{12}H_8N_2Fe_2(CO)_6$ was generously supplied by Dr. R. P. Bennett of the American Cyanamid Corp. Suitable single crystals could be prepared either by sublimation at reduced pressures or by recrystallization from acetone, with the latter method yielding larger and better formed crystals. Preliminary X-ray photographs confirmed that the crystals ob-

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[1] Presented in part at the Fourth International Conference on Organometallic Chemistry, Bristol, England, Aug 1969.

[2] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **8**, 2709 (1969).

[3] M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967); G. R. Knox, private communication.

[4] P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, **1**, 55 (1967).

[5] M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Commun.*, 1106 (1967).

[6] J. Piron, P. Piret, and M. Van Meerssche, *Bull. Soc. Chim. Belg.*, **76**, 505 (1967).

[7] J. A. J. Jarvis, B. E. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967).

[8] L. F. Dahl, W. R. Costello, and R. B. King, *J. Amer. Chem. Soc.*, **90**, 5422 (1968).

[9] R. J. Doedens, *Inorg. Chem.*, **7**, 2323 (1968).

[10] R. P. Bennett, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, and private communication.

[11] C. D. Campbell and C. W. Rees, *Chem. Commun.*, 537 (1969).

tained by the two methods have identical unit cell constants and revealed no evidence of monoclinic or higher symmetry. A Delaunay reduction supported the assignment of this material to the triclinic crystal system. Lattice parameters were obtained by the least-squares refinement of the setting angles of 14 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. For the centering of reflections, the takeoff angle was set at 0.7°. The unit cell constants (23°, λ(Mo Kα_1) 0.70930 Å) obtained in this manner are $a = 7.892$ (12) Å, $b = 9.037$ (14) Å, $c = 14.884$ (24) Å, $\alpha = 86° \, 32'$ (2′), $\beta = 113° \, 39'$ (2′), and $\gamma = 107° \, 0'$ (2′). The numbers in parentheses are the standard deviations obtained from the least-squares refinement of the setting angles. The density of 1.645 g/cm^3 calculated on the basis of two formula units per cell agrees well with the value of 1.64 (2) g/cm^3 observed by flotation in aqueous zinc bromide solution. The centrosymmetric space group C_i^1-$P\bar{1}$ was assumed; no evidence arose during the course of the structural determination to contradict this assumption. In space group $P\bar{1}$ with $Z = 2$, the asymmetric unit contains one molecule, and thus no molecular symmetry is required.

Intensity data were collected from a well-formed tabular crystal of dimensions 0.37 × 0.31 × 0.16 mm mounted in a thin-walled glass capillary roughly parallel to its longest dimension (the crystallographic $[01\bar{2}]^*$ direction). The 0.16-mm dimension was perpendicular to the well-developed $\{1\bar{1}\bar{1}\}$ faces; other bounding planes were $\{01\bar{1}\}$, $\{001\}$, $\{100\}$, and $\{011\}$. The data were collected on a Picker automatic diffractometer by use of procedures previously described in detail.[12] The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperture was 4 mm square and was positioned 29.5 cm from the crystal. Data were collected by the θ–2θ scan method; a symmetric scan range of ±0.6° in 2θ from the calculated scattering angle was used for all reflections having $2\theta \leq 30°$. For reflections with $2\theta > 30°$, an additional 0.1° in 2θ was added to the high end of the scan range. The scan rate was 1.0°/min, and 10-sec background counts were taken at each end of the scan. Copper foil attenuators were automatically inserted in the path of the diffracted beam whenever the counting rate exceeded ~7000 counts/sec. Three standard reflections, chosen to lie in widely separated regions of the reciprocal lattice, were monitored regularly through the collection of the data. An abrupt and significant drop of ~20% in the intensities of *one* of these standard reflections was observed early in the data collection run. Careful recentering of several reflections indicated that the crystal had moved by a small amount and that the motion was very nearly a pure ϕ rotation which could be compensated for by adding 0.18° to the calculated ϕ values for all reflections collected subsequent to the last normal measurement of the standard reflections. The fact that only one of three standard reflections was affected in this incident underscores the advisability of using several carefully chosen standard reflections to monitor the crystal and electronic stability during a diffractometer data collection run. No further variation in the intensities of any of the standard reflections occurred. Data were collected for all independent reflections with $\theta \leq 22.5°$; the intensities of a total of 2444 reflections were measured within this limiting value of the Bragg angle. Beyond $\theta = 22.5°$ only a small fraction (<20%) of the intensities were above background.

Previously described methods[12] were employed in the processing of the intensity data. The factor p in the expression for the standard deviations was assigned a value of 0.05. Of the 2444 independent intensities measured, 1970 had intensities above background by three or more standard deviations. The observed intensities were corrected for absorption; based upon a linear absorption coefficient of 16.9 cm^{-1}, the calculated transmission factors ranged from 0.69 to 0.82.

Solution and Refinement of the Structure

The solution of the structure was accomplished by standard heavy-atom methods. A three-dimensional Patterson function, interpreted on the assumption of the centrosymmetric space group $P\bar{1}$, yielded a consistent set of trial coordinates for the two iron atoms. Least-squares refinement of these coordinates, individual isotropic atomic temperature factors, and a scale factor yielded discrepancy factors $R_1 = 100\Sigma||F_o| - |F_c||/\Sigma|F_o| = 41.5\%$ and $R_2 = 100[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 50.9\%$. In this and subsequent refinements, only the intensity data with $F_o^2 \geq 3\sigma(F_o^2)$ were used. A difference Fourier map phased on the refined iron coordinates yielded the positions of the 26 carbon, nitrogen, and oxygen atoms. Refinement of positional and isotropic thermal parameters for all atoms (based upon a randomly chosen half of the intensity data[13] to conserve computer time) converged to $R_1 = 9.1\%$ and $R_2 = 12.7\%$. Further refinement with anisotropic temperature factors for the iron atoms significantly lowered R_1 and R_2 to 6.2 and 8.7%, respectively. A difference Fourier map calculated at this point showed no positive peaks of height greater than 0.35 e$^-$/Å^3. The "ideal" positions (on the bisector of the ring angle with C–H = 1.08 Å) of the eight hydrogen atoms were calculated and compared with the difference map. A positive peak was found at each of the eight calculated locations; the peak heights ranged from 0.13 to 0.35 e$^-$/Å^3. The hydrogen atoms were included in the final cycles of refinement as fixed atoms at their calculated positions, with isotropic temperature factors of 7.0 Å^2. The final refinement was based upon all 1970 data with $F_o^2 > 3\sigma(F_o^2)$ and employed the same thermal model

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[12] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[13] The random selection of half of the intensity data was based upon an "even–odd" test of the least significant digit of the observed F^2 value. It is unlikely that such a procedure will introduce appreciable bias into the selection.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS FOR $C_{12}H_8N_2Fe_2(CO)_6$

K	L	FO	FC
***** H = 0 *****			
0	1	280	236
0	2	632	580
0	3	793	806
0	5	628	568
0	6	232	242
0	7	307	281
0	8	345	338
0	9	217	219
0	11	128	118
1	0	82	66
1	1	846	764
1	2	855	812
1	3	115	105
1	4	75	37
1	5	102	119
1	6	95	90
1	7	351	364
1	8	239	241
1	9	148	153
1	10	354	337
1	11	134	137
1	12	49	67
1	13	130	139
1	-1	1147	1312
1	-2	716	718
1	-3	507	485
1	-4	678	674
1	-5	541	518
1	-6	443	433
1	-7	200	217
1	-8	98	93
1	-9	145	142
1	-11	81	47
1	-12	105	97
1	-13	81	89
1	-14	52	35
2	0	785	803
2	1	446	455
2	2	322	287
2	3	252	253
2	4	90	95
2	5	446	405
2	6	464	476
2	7	347	329
2	8	235	240
2	9	483	485
2	10	55	53
2	11	253	238
2	12	273	253
2	14	111	113
2	-1	242	231
2	-3	233	217
2	-4	253	241
2	-5	85	88
2	-6	203	229
2	-7	200	198
2	-10	95	91
2	-11	104	106
2	-12	86	85
2	-13	82	79
2	-14	161	143
3	0	382	369
3	1	86	92
3	2	705	696
3	3	50	60
3	4	205	211
3	5	348	326
3	6	141	125
3	7	333	326
3	8	329	330
3	9	162	158
3	10	524	503
3	11	165	174
3	12	46	59
3	13	208	205
3	-1	27	16
3	-3	108	107
3	-7	50	25
3	-8	128	113
3	-9	267	243
3	-10	166	156
3	-12	174	179
3	-13	87	101
3	-14	165	137
4	0	100	110
4	1	188	196
4	2	124	123
4	3	41	11
4	4	385	394
4	5	95	79
4	6	238	244
4	7	226	232
4	8	50	47
4	9	482	475
4	11	120	134
4	12	243	213
4	-1	39	49
4	-3	386	377
4	-4	299	280
4	-5	210	200
4	-6	138	144
4	-7	196	172
4	-8	320	314
4	-11	181	206
4	-13	211	197
5	1	260	273
5	2	97	124
5	3	81	56
5	4	94	97
5	5	131	135
5	6	81	81
5	7	108	97
5	8	138	126
5	9	65	67
5	10	107	116
5	11	162	144
5	-1	78	78
5	-2	130	134
5	-3	136	132
5	-4	301	288
5	-5	48	41
5	-6	323	319
5	-7	206	202
5	-8	50	48
5	-9	342	353
5	-12	197	169
6	0	147	144
6	1	319	310
6	2	53	45
6	3	170	160
6	4	122	104
6	5	74	71
6	9	69	59
6	10	47	54
6	-1	148	156
6	-2	251	263
6	-3	145	142
6	-4	252	253
6	-5	254	245
6	-6	60	54
6	-7	252	252
6	-8	226	219
6	-10	139	129
6	-11	114	115
7	0	175	170
7	1	63	53
7	2	145	167
7	3	166	173
7	4	48	47
7	6	72	70
7	-1	147	163
7	-2	117	107
7	-3	278	273
7	-4	143	166
7	-5	157	159
7	-6	257	268
7	-7	54	53
7	-8	142	141
7	-9	134	147
8	0	140	174
8	1	217	228
8	2	115	115
8	3	83	74
8	4	167	170
8	5	73	91
8	6	146	127
8	-2	130	138
8	-4	144	151
8	-5	132	134
8	-7	148	165
8	-8	47	37
9	0	182	170
9	1	71	76
9	2	103	104
9	-2	78	69
9	-3	101	92
***** H = 1 *****			
0	0	813	754
0	1	58	64
0	2	573	578
0	3	182	172
0	4	385	380
0	5	107	112
0	6	46	56
0	7	202	186
0	8	91	102
0	12	90	96
0	-1	456	401
0	-2	943	956
0	-3	431	437
0	-4	975	1035
0	-5	1118	1146
0	-6	58	50
0	-7	275	316
0	-8	454	507
0	-9	158	168
0	-10	340	319
0	-11	440	417
0	-12	69	29
0	-13	120	137
0	-14	83	83
1	0	819	867
1	1	140	117
1	2	432	414
1	3	373	365
1	4	178	153
1	5	399	394
1	6	126	121
1	7	85	84
1	8	84	95
1	9	111	98
1	10	80	73
1	11	74	60
1	12	52	31
1	13	45	46
1	-1	837	848
1	-2	111	117
1	-3	856	925
1	-4	54	43
1	-5	798	824
1	-6	722	740
1	-7	98	93
1	-8	372	356
1	-9	571	569
1	-10	189	163
1	-11	173	186
1	-12	189	205
1	-13	40	5
1	-14	43	50
1	-15	82	70
2	0	1024	1080
2	1	1205	1263
2	2	250	243
2	3	131	124
2	4	364	367
2	5	66	66
2	6	255	288
2	7	196	191
2	8	178	180
2	9	211	194
2	10	163	161
2	12	48	49
2	-1	55	39
2	-2	867	902
2	-3	85	89
2	-4	664	677
2	-5	579	548
2	-6	140	142
2	-7	362	376
2	-8	312	310
2	-9	159	162
2	-10	269	262
2	-11	63	82
2	-12	59	36
2	-13	65	49
3	0	693	658
3	1	140	154
3	2	247	269
3	3	308	317
3	4	335	312
3	5	278	287
3	6	319	349
3	8	367	357
3	9	269	264
3	10	223	221
3	11	95	91
3	12	82	74
3	-1	604	605
3	-2	320	275
3	-3	484	470
3	-4	80	88
3	-5	106	102
3	-6	368	377
3	-7	221	223
3	-8	149	129
3	-9	225	262
3	-10	69	50
3	-11	292	268
3	-12	40	59
3	-13	57	55
3	-14	63	48
4	0	61	63
4	1	456	484
4	2	368	384
4	3	35	63
4	4	445	441
4	5	252	259
4	6	187	175
4	7	445	435
4	8	169	158
4	9	168	163
4	10	201	195
4	11	83	80
4	-1	294	309
4	-2	238	223
4	-3	275	281
4	-6	104	127
4	-7	38	46
4	-9	158	148
4	-13	46	56
5	0	324	321
5	1	208	214
5	2	200	210
5	3	298	309
5	4	215	212
5	5	117	114
5	6	285	268
5	7	125	109
5	8	142	151
5	9	199	203
5	-2	242	241
5	-3	36	51
5	-4	137	158
5	-5	51	59
5	-7	61	47
5	-8	159	141
5	-9	165	159
5	-10	47	77
5	-12	71	74
5	-13	115	96
6	0	47	53
6	1	96	94
6	2	129	129
6	4	120	136
6	5	70	72
6	7	110	121
6	8	82	98
6	9	43	37
6	-1	90	135
6	-2	166	165
6	-3	62	62
6	-4	176	165
6	-5	85	80
6	-6	121	121
6	-7	216	210
6	-8	71	71
6	-9	103	93
6	-10	111	127
7	0	110	94
7	3	36	17
7	6	38	30
7	7	82	92
7	-1	69	72
7	-2	63	53
7	-3	145	149
7	-4	81	90
7	-5	172	167
7	-6	99	94
7	-7	81	76
7	-8	225	224
7	-10	82	64
8	0	71	83
8	1	123	124
8	2	56	54
8	4	54	47
8	-1	69	45
8	-3	75	85
8	-4	64	71
8	-6	79	88
8	-7	107	112
-1	0	396	359
-1	1	590	542
-1	2	155	147
-1	3	89	96
-1	4	44	32
-1	5	438	409
-1	6	278	255
-1	7	295	286
-1	10	166	154
-1	11	194	192
-1	13	177	191
-1	-1	727	671
-1	-2	218	207
-1	-3	24	23
-1	-4	592	599
-1	-5	57	61
-1	-6	358	358
-1	-7	291	280
-1	-8	292	243
-1	-9	442	443
-1	-10	279	275
-1	-11	86	95
-1	-12	283	271
-1	-13	111	121
-1	-14	50	56
-1	-15	216	207
-2	0	35	29
-2	1	104	104
-2	2	287	295
-2	3	301	315
-2	4	262	264
-2	5	76	95
-2	6	691	683
-2	7	243	261
-2	8	276	252
-2	9	487	463
-2	10	205	183
-2	11	117	131
-2	12	229	247
-2	-1	457	461
-2	-2	304	270
-2	-3	487	487
-2	-4	67	74
-2	-5	416	392
-2	-6	185	168
-2	-7	190	190
-2	-8	361	349
-2	-9	109	124
-2	-10	270	250
-2	-11	378	368
-2	-12	124	119
-2	-13	166	189
-2	-14	169	187
-3	0	232	244
-3	1	287	292
-3	2	272	264
-3	4	394	388
-3	5	367	337
-3	6	72	86
-3	7	472	482
-3	8	328	309
-3	9	46	76
-3	10	334	337
-3	11	186	199
-3	12	86	80
-3	13	249	218
-3	-1	233	252
-3	-2	336	334
-3	-3	41	42
-3	-4	115	117
-3	-5	197	208
-3	-6	67	62
-3	-7	144	139
-3	-9	132	137
-3	-10	298	273
-3	-12	178	178
-3	-13	184	176
-3	-14	40	32
-4	0	420	393
-4	1	184	185
-4	2	141	139
-4	3	388	367
-4	4	61	63
-4	5	196	214
-4	6	320	322
-4	8	192	180
-4	9	277	295
-4	10	85	79
-4	11	204	200
-4	12	170	162
-4	-1	110	108
-4	-2	306	308
-4	-3	725	714
-4	-4	73	64
-4	-5	155	147
-4	-6	54	50
-4	-7	46	49
-4	-9	203	200
-4	-10	57	55
-4	-11	186	180
-4	-13	69	74
-5	1	268	272
-5	2	394	405
-5	3	52	53
-5	4	565	580
-5	5	127	127
-5	6	223	212
-5	7	277	282
-5	8	42	25
-5	9	156	158
-5	11	132	147
-5	12	76	76
-5	-1	402	431
-5	-2	585	583
-5	-3	74	62
-5	-4	399	395
-5	-5	85	73
-5	-6	158	163
-5	-7	69	69
-5	-8	60	33
-5	-10	48	57
-5	-11	142	133
-5	-12	54	55
-6	0	373	369
-6	1	118	123
-6	2	159	157
-6	3	398	406
-6	5	293	295
-6	6	234	230
-6	8	203	210
-6	10	83	87
-6	-1	183	185
-6	-2	169	172
-6	-3	459	478
-6	-4	170	180
-6	-5	157	141
-6	-6	272	261
-6	-7	50	29
-6	-8	117	114
-6	-9	158	148
-6	-10	64	53
-6	-11	88	82
-7	0	127	111
-7	1	218	213
-7	2	127	124
-7	3	127	128
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-1	-13	186	192
-1	-15	159	132
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-2	1	205	185
-2	2	374	361
-2	3	229	237
-2	4	73	91
-2	6	45	40
-2	8	90	96
-2	9	56	32
-2	-1	83	99
-2	-2	183	200
-2	-3	564	604
-2	-4	156	176
-2	-5	280	263
-2	-6	408	421
-2	-7	44	30
-2	-8	377	389
-2	-9	430	438
-2	-10	96	80
-2	-11	392	385
-2	-12	348	341
-2	-14	179	196
-2	-15	106	109
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-3	2	66	53
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-3	5	44	37
-3	6	60	68
-3	7	86	90
-3	8	38	22
-3	9	77	75
-3	-2	377	377
-3	-3	110	75
-3	-4	135	143
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-3	-7	306	323
-3	-8	412	396
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-3	-10	361	347
-3	-11	254	241
-3	-12	126	135
-3	-13	223	245
-3	-14	90	105
-3	-15	218	195
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-4	2	172	190
-4	3	216	201
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-4	7	73	78
-4	8	162	169
-4	9	72	75
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-4	-2	359	324
-4	-3	350	351
-4	-4	74	32
-4	-5	198	206
-4	-6	388	384
-4	-7	161	171
-4	-8	371	351
-4	-9	166	197
-4	-10	99	102
-4	-11	133	128
-4	-12	208	217
-4	-14	174	186
-4	-15	108	105
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-5	6	142	147
-5	7	178	167
-5	-1	56	64
-5	-2	121	131
-5	-3	112	107
-5	-4	63	63
-5	-5	147	167
-5	-6	87	93
-5	-10	46	53
-5	-11	94	87
-5	-12	60	45
-5	-13	121	128
-5	-14	99	106
-6	0	173	181
-6	1	80	80
-6	2	290	290
-6	3	104	97
-6	4	193	197
-6	5	190	214
-6	6	91	89
-6	7	93	65
-6	8	126	129
-6	-1	286	282
-6	-2	41	54
-6	-3	171	163
-6	-4	135	124
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-6	-6	94	84
-6	-7	55	60
-6	-12	37	32
-6	-13	72	66
-7	0	190	181
-7	1	209	195
-7	3	201	196
-7	4	152	140
-7	6	151	158
-7	-1	71	75
-7	-2	258	250
-7	-3	98	83
-7	-4	167	167
-7	-5	83	84
-7	-6	55	68
-7	-7	56	51
-7	-8	72	73
-7	-11	162	144
-8	0	129	144
-8	1	169	165
-8	2	91	80
-8	4	70	64
-8	5	85	82
-8	-1	204	213
-8	-2	77	92
-8	-3	127	128
-8	-4	121	116
-8	-5	122	116
-8	-6	146	155
-8	-7	132	134
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-9	0	134	138
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-9	2	62	67
-9	-1	55	62
-9	-2	82	89
-9	-3	125	130
-9	-5	115	116
-9	-6	118	111
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0	6	81	94
0	7	84	65
0	-1	222	219
0	-2	317	331
0	-3	51	74
0	-4	120	131
0	-5	407	404
0	-7	417	415
0	-8	248	249
0	-9	96	92
0	-10	298	286
0	-11	110	112
0	-13	61	83
0	-14	120	159
0	-15	123	118
1	0	226	208
1	1	40	22
1	2	112	123
1	3	64	70
1	-1	216	212
1	-2	126	131
1	-3	325	338
1	-4	252	243
1	-5	170	164
1	-6	408	426
1	-7	99	95
1	-8	276	277
1	-9	325	314
1	-10	82	64
1	-11	203	212
1	-12	68	93
1	-14	141	116
1	-15	44	45
2	1	209	223
2	2	111	107
2	4	138	159
2	5	69	65
2	-1	278	279
2	-2	186	148
2	-4	329	336
2	-5	252	250
2	-6	77	64
2	-7	288	292
2	-8	143	144
2	-9	120	115
2	-10	202	187
2	-11	75	78
2	-12	38	51
3	0	232	228
3	1	128	155
3	2	80	70
3	3	212	219
3	4	56	82
3	5	121	111
3	-2	145	168
3	-3	105	85
3	-4	125	125
3	-5	305	290
3	-6	183	176
3	-8	190	180
3	-9	168	176
3	-10	45	42
4	1	157	161
4	2	205	199
4	-1	174	194
4	-2	65	83
4	-3	79	72
4	-6	56	70
4	-7	72	58
4	-9	63	53
4	-10	62	51
4	-11	39	41
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5	1	96	93
5	-2	51	69
5	-3	46	40
5	-8	41	32
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-1	2	67	65
-1	4	71	61
-1	6	76	77
-1	7	52	50
-1	-1	87	96
-1	-2	101	110
-1	-3	266	278
-1	-4	202	191
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-1	-7	65	79
-1	-8	157	148
-1	-9	331	334
-1	-10	163	140
-1	-11	151	154
-1	-12	159	191
-1	-13	189	188
-1	-14	277	262
-1	-15	195	184
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-2	1	76	67
-2	3	138	120
-2	4	64	56
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-2	6	68	78
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-2	8	64	67
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-2	-5	265	282
-2	-6	166	173
-2	-7	87	95
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-2	-9	60	66
-2	-10	168	171
-2	-11	180	177
-2	-13	189	190
-2	-14	183	188
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-3	1	99	87
-3	2	184	177
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-3	8	195	189
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-3	-5	63	75
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-3	-13	54	69
-3	-14	47	35
-3	-15	214	195
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-4	7	120	118
-4	-1	159	212
-4	-2	456	474
-4	-3	303	325
-4	-4	76	79
-4	-5	206	208
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-4	-7	88	80
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-4	-10	49	65
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-5	4	140	154
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-5	-2	191	178
-5	-3	327	331
-5	-4	162	171
-5	-5	140	149
-5	-6	134	117
-5	-7	125	99
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-5	-11	72	72
-5	-12	38	19
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-6	-1	173	199
-6	-2	315	293
-6	-3	174	183
-6	-5	221	218
-6	-6	154	161
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-6	-10	39	47
-6	-11	103	108
-6	-12	69	56
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-7	-1	140	143
-7	-2	182	193
-7	-4	164	160
-7	-5	108	102
-7	-7	157	158
-7	-8	104	94
-7	-9	70	66
-7	-10	139	146
-7	-11	120	101
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-8	3	67	69
-8	-1	138	140
-8	-3	148	137
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-8	-6	179	175
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-8	-8	115	103
-8	-9	177	168
-9	-2	72	64
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-9	-4	48	32
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0	2	110	121
0	4	68	73
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0	-4	98	96
0	-5	90	99
0	-6	96	88
0	-7	146	155
0	-8	75	89
0	-9	174	176
0	-10	133	139
0	-11	74	69
0	-12	165	179
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0	-14	44	29
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1	1	65	65
1	-2	45	53
1	-3	71	70
1	-5	168	165
1	-6	112	106
1	-7	135	138
1	-8	235	228
1	-9	117	116
1	-10	147	153
1	-11	179	192
1	-13	108	94
1	-14	158	154
2	3	72	67
2	-1	115	127
2	-3	57	55
2	-4	248	261
2	-6	225	220
2	-7	169	172
2	-9	268	280
2	-10	114	100
2	-11	74	72
2	-12	117	129
2	-13	66	67
3	0	54	40
3	1	112	106
3	-1	76	71
3	-2	182	184
3	-5	146	153
3	-6	75	73
3	-7	164	171
3	-8	174	166
3	-9	45	49
3	-10	194	212
3	-11	80	79
4	-1	107	108
4	-3	131	119
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4	-5	92	86
4	-6	44	82
4	-7	41	42
4	-8	56	66
4	-9	80	87
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-1	3	152	158
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-1	-1	125	127
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-1	-3	120	113
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-1	-5	55	55
-1	-6	119	116
-1	-7	129	131
-1	-8	92	93
-1	-10	41	53
-1	-11	139	147
-1	-12	128	116
-1	-13	45	46
-1	-14	192	172
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-2	1	95	105
-2	2	173	171
-2	4	163	149
-2	5	132	116
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-2	-2	219	208
-2	-4	178	166
-2	-6	60	55
-2	-7	119	122
-2	-9	76	58
-2	-12	44	44
-2	-13	101	103
-2	-14	60	45
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-3	5	137	125
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-3	-2	141	150
-3	-3	363	376
-3	-4	114	103
-3	-5	230	231
-3	-6	192	186
-3	-8	216	217
-3	-9	127	127
-3	-10	84	85
-3	-11	130	135
-3	-12	90	72
-4	0	150	176
-4	1	184	209
-4	2	173	181
-4	3	73	67
-4	4	177	167
-4	5	68	71
-4	-1	138	124
-4	-2	309	305
-4	-3	47	43
-4	-4	305	298
-4	-5	311	323
-4	-6	104	90
-4	-7	262	240
-4	-8	109	110
-4	-9	131	125
-4	-10	191	193
-4	-11	79	75
-4	-13	49	64
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-5	2	107	110
-5	3	86	70
-5	5	51	49
-5	-1	145	154
-5	-2	61	70
-5	-3	349	342
-5	-4	63	48
-5	-5	200	209
-5	-6	197	205
-5	-7	77	74
-5	-8	164	166
-5	-9	107	118
-5	-10	138	135
-5	-11	116	121
-5	-12	138	131
-5	-13	45	29
-6	1	74	82
-6	3	59	55
-6	4	47	36
-6	-2	205	213
-6	-3	119	137
-6	-4	41	64
-6	-5	214	236
-6	-6	71	72
-6	-7	149	154
-6	-8	167	166
-6	-9	105	96
-6	-10	193	183
-6	-11	185	169
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-7	-3	55	63
-7	-4	110	99
-7	-6	150	142
-7	-7	168	172
-7	-9	146	127
-7	-10	137	132
-8	-5	60	51
-8	-6	54	53
-8	-6	81	79
***** H = 7 *****			
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0	-1	95	97
0	-3	197	207
0	-4	65	47
0	-5	75	64
0	-6	119	113
0	-9	40	31
0	-10	37	35
1	-1	43	66
1	-2	99	100
1	-4	156	168
1	-5	70	73
1	-7	34	14
1	-10	67	80
1	-11	40	42
1	-12	59	56
2	-2	75	72
2	-3	53	70
2	-5	80	69
2	-6	51	68
2	-7	73	72
2	-8	48	42
2	-9	99	95
-1	0	56	68
-1	1	173	177
-1	2	84	90
-1	-1	136	134
-1	-2	188	192
-1	-3	101	105
-1	-4	147	144
-1	-5	202	203
-1	-7	130	129
-1	-8	103	106
-1	-10	77	77
-1	-11	57	69
-1	-12	77	58
-1	-13	57	58
-2	0	121	102
-2	2	167	165
-2	3	99	110
-2	-1	135	130
-2	-3	188	196
-2	-4	241	240
-2	-5	88	69
-2	-6	174	160
-2	-7	108	106
-2	-8	71	76
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-2	-10	70	72
-2	-11	45	60
-2	-12	138	140
-3	0	100	95
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-3	3	68	65
-3	-2	203	199
-3	-3	60	52
-3	-4	125	127
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-3	-6	86	78
-3	-7	130	141
-3	-8	269	271
-3	-10	172	166
-3	-11	133	139
-3	-13	159	164
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-4	-1	115	118
-4	-3	97	111
-4	-4	150	175
-4	-5	43	57
-4	-6	108	110
-4	-7	206	216
-4	-9	161	155
-4	-10	174	168
-4	-12	154	155
-4	-13	70	87
-5	-3	50	45
-5	-5	97	103
-5	-6	125	121
-5	-8	175	154
-5	-9	90	72
-5	-10	49	71
-5	-11	155	153
-5	-12	62	57
-6	0	49	49
-6	-2	96	89
-6	-3	77	78
-6	-4	45	37
-6	-5	42	54
-6	-7	90	83
-6	-9	57	58
-6	-10	131	123
-7	-4	113	103
-7	-5	51	58
***** H = 8 *****			
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0	-5	86	79
0	-6	70	75
0	-7	68	70
0	-8	151	162
0	-9	48	36
-1	-2	52	37
-1	-3	115	108
-1	-4	151	160
-1	-6	107	109
-1	-7	138	146
-1	-9	134	144
-1	-10	106	111
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-2	-3	83	81
-2	-4	55	45
-2	-5	117	116
-2	-6	71	77
-2	-8	117	113
-2	-9	101	91
-2	-11	108	115
-3	-2	38	17
-3	-4	52	95
-3	-6	55	58
-3	-7	45	34
-3	-8	134	126
-3	-10	167	169
-3	-11	59	53
-4	-6	42	42
-4	-7	87	88
-4	-8	64	56
-4	-9	117	118
-4	-10	45	47

Table II

Atomic Positional and Thermal Parameters for $C_{12}H_8N_2Fe_2(CO)_6$[a]

	x	y	z	B, Å²
Fe(1)	0.26957 (14)	−0.28171 (12)	−0.16003 (7)	. . .
Fe(2)	0.00295 (14)	−0.16104 (11)	−0.19428 (7)	. . .
C(1–1)	0.4712 (11)	−0.1159 (9)	−0.1177 (6)	5.02 (16)
O(1–1)	0.6020 (10)	−0.0060 (8)	−0.0937 (5)	7.63 (15)
C(1–2)	0.3035 (13)	−0.3502 (11)	−0.0437 (7)	5.87 (19)
O(1–2)	0.3199 (12)	−0.3988 (10)	0.0332 (6)	9.24 (20)
C(1–3)	0.3776 (12)	−0.4019 (10)	−0.1971 (6)	4.95 (17)
O(1–3)	0.4511 (10)	−0.4739 (8)	−0.2219 (5)	7.37 (17)
C(2–1)	0.1319 (11)	0.0377 (9)	−0.1660 (6)	5.07 (16)
O(2–1)	0.2203 (10)	0.1686 (8)	−0.1483 (5)	7.43 (16)
C(2–2)	−0.0336 (11)	−0.1910 (9)	−0.0835 (6)	5.27 (17)
O(2–2)	−0.0559 (10)	−0.2137 (8)	−0.0108 (5)	7.94 (17)
C(2–3)	−0.2267 (12)	−0.1411 (9)	−0.2720 (6)	4.68 (16)
O(2–3)	−0.3765 (10)	−0.1276 (8)	−0.3219 (5)	7.09 (15)
N(1)	−0.0020 (8)	−0.3579 (6)	−0.2373 (4)	3.56 (11)
N(2)	0.0868 (7)	−0.2373 (6)	−0.2818 (4)	3.43 (10)
RC(1)	0.0397 (9)	−0.2486 (7)	−0.3836 (5)	3.31 (12)
RC(2)	0.1453 (11)	−0.1310 (9)	−0.4215 (6)	4.58 (15)
RC(3)	0.0965 (12)	−0.1386 (10)	−0.5217 (6)	5.30 (17)
RC(4)	−0.0519 (13)	−0.2587 (11)	−0.5812 (7)	5.60 (19)
RC(5)	−0.1548 (11)	−0.3742 (9)	−0.5435 (6)	4.78 (16)
RC(6)	−0.1091 (10)	−0.3730 (8)	−0.4414 (5)	3.60 (13)
RC(7)	−0.1437 (10)	−0.4923 (8)	−0.2942 (5)	3.67 (13)
RC(8)	−0.2182 (12)	−0.6099 (10)	−0.2428 (6)	5.00 (18)
RC(9)	−0.3612 (15)	−0.7394 (12)	−0.2991 (8)	6.43 (22)
RC(10)	−0.4273 (14)	−0.7476 (12)	−0.3969 (7)	6.24 (21)
RC(11)	−0.3551 (12)	−0.6297 (10)	−0.4481 (6)	5.18 (17)
RC(12)	−0.2062 (10)	−0.4982 (8)	−0.3960 (5)	3.87 (15)
HRC(2)	0.2659	−0.0401	−0.3721	[b]
HRC(3)	0.1792	−0.0479	−0.5541	. . .
HRC(4)	−0.0939	−0.2651	−0.6598	. . .
HRC(5)	−0.2785	−0.4646	−0.5927	. . .
HRC(8)	−0.1665	−0.5990	−0.1627	. . .
HRC(9)	−0.4142	−0.8405	−0.2627	. . .
HRC(10)	−0.5404	−0.8485	−0.4368	. . .
HRC(11)	−0.4192	−0.6353	−0.5283	. . .

Anisotropic Thermal Parameters ($\times 10^5$)[c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	2010 (28)	1634 (19)	363 (6)	546 (17)	239 (10)	35 (8)
Fe(2)	2175 (28)	1341 (17)	449 (7)	423 (16)	442 (10)	−51 (8)

[a] Numbers in parentheses in tables and in the text are standard deviations in the least significant figures. [b] Hydrogen atoms were arbitrarily assigned isotropic temperature factors of 7.0 Å². [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

as was used in the previous round of calculations. This refinement converged to $R_1 = 6.0\%$ and $R_2 = 8.5\%$, with no parameter shifting by as much as 0.1σ in the last cycle.

The final standard deviation of an observation of unit weight was 2.57. This value would undoubtedly have been lower had a full anisotropic refinement been carried out and may also indicate an underestimation of the scale of the standard deviations of the observed intensities. Calculation of $w(\Delta F)^2$ for subsets of the data as a function of uncorrected intensity, observed F, and Bragg angle showed no significant trends; thus confirming that the relative weights were appropriate. Calculation of structure factors for data with $F_o^2 \leq 3\sigma(F_o^2)$ revealed five reflections with $F_c > 3\sigma(F_o)$; of these, only one had $F_o > 4\sigma(F_o)$.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The scattering factors for Fe, C, N, and O tabulated by Ibers[14a] and those for H of Stewart, *et al.*,[14b] were used in all structure factor calculations.

Table III

Intramolecular Distances (Å)

Fe(1)–Fe(2)	2.508 (4)	N(1)–N(2)	1.399 (8)
Fe(1)–N(1)	1.910 (6)	Fe(2)–N(1)	1.912 (6)
Fe(1)–N(2)	1.918 (6)	Fe(2)–N(2)	1.917 (6)
Mean Fe–N	1.914 (3)		
Fe(1)–C(1–1)	1.758 (8)	Fe(2)–C(2–1)	1.766 (9)
Fe(1)–C(1–2)	1.745 (10)	Fe(2)–C(2–2)	1.777 (9)
Fe(1)–C(1–3)	1.789 (9)	Fe(2)–C(2–3)	1.772 (8)
Mean Fe–C	1.768 (4)		
N(1)–RC(7)	1.419 (9)	N(2)–RC(1)	1.410 (8)
Mean N–C	1.414 (6)		
RC(7)–RC(8)	1.399 (11)	RC(1)–RC(2)	1.389 (10)
RC(8)–RC(9)	1.391 (12)	RC(2)–RC(3)	1.384 (11)
RC(9)–RC(10)	1.333 (13)	RC(3)–RC(4)	1.369 (12)
RC(10)–RC(11)	1.391 (13)	RC(4)–RC(5)	1.365 (12)
RC(11)–RC(12)	1.400 (11)	RC(5)–RC(6)	1.414 (11)
RC(12)–RC(7)	1.392 (10)	RC(6)–RC(1)	1.385 (9)
Mean C–C (ring)	1.384 (4)		
C(1–1)–O(1–1)	1.152 (9)	C(2–1)–O(2–1)	1.168 (10)
C(1–2)–O(1–2)	1.173 (11)	C(2–2)–O(2–2)	1.162 (10)
C(1–3)–O(1–3)	1.149 (10)	C(2–3)–O(2–3)	1.155 (9)
Mean C–O	1.159 (4)		
RC(6)–RC(12)	1.462 (10)		
C(1–1)···C(1–2)	2.588 (13)	C(2–1)···C(2–2)	2.624 (12)
C(1–1)···C(1–3)	2.678 (12)	C(2–1)···C(2–3)	2.676 (12)
C(1–2)···C(1–3)	2.669 (13)	C(2–2)···C(2–3)	2.687 (12)
N(1)···C(1–2)	2.911 (11)	N(2)···C(1–1)	2.968 (10)
N(1)···C(1–3)	2.953 (11)	N(2)···C(1–3)	2.919 (11)
N(1)···C(2–2)	2.944 (11)	N(2)···C(2–1)	2.963 (10)
N(1)···C(2–3)	2.903 (10)	N(2)···C(2–3)	2.909 (10)

Table IV

Bond Angles (Deg)

Fe(2)–Fe(1)–N(1)	49.0 (2)	Fe(1)–Fe(2)–N(1)	48.9 (2)
Fe(2)–Fe(1)–N(2)	49.1 (2)	Fe(1)–Fe(2)–N(2)	49.2 (2)
Fe(2)–Fe(1)–C(1–1)	100.1 (3)	Fe(1)–Fe(2)–C(2–1)	102.0 (3)
Fe(2)–Fe(1)–C(1–2)	102.4 (3)	Fe(1)–Fe(2)–C(2–2)	100.9 (3)
Fe(2)–Fe(1)–C(1–3)	151.2 (3)	Fe(1)–Fe(2)–C(2–3)	150.3 (3)
N(1)–Fe(1)–N(2)	42.9 (2)	N(1)–Fe(2)–N(2)	42.9 (2)
N(1)–Fe(1)–C(1–1)	145.4 (3)	N(1)–Fe(2)–C(2–1)	146.1 (3)
N(1)–Fe(1)–C(1–2)	105.5 (3)	N(1)–Fe(2)–C(2–2)	105.9 (3)
N(1)–Fe(1)–C(1–3)	105.9 (3)	N(1)–Fe(2)–C(2–3)	103.9 (3)
N(2)–Fe(1)–C(1–1)	107.6 (3)	N(2)–Fe(2)–C(2–1)	107.1 (3)
N(2)–Fe(1)–C(1–2)	145.5 (3)	N(2)–Fe(2)–C(2–2)	145.1 (3)
N(2)–Fe(1)–C(1–3)	103.8 (3)	N(2)–Fe(2)–C(2–3)	104.0 (3)
C(1–1)–Fe(1)–C(1–2)	95.2 (4)	C(2–1)–Fe(2)–C(2–2)	95.6 (4)
C(1–1)–Fe(1)–C(1–3)	98.0 (4)	C(2–1)–Fe(2)–C(2–3)	98.3 (4)
C(1–2)–Fe(1)–C(1–3)	98.1 (4)	C(2–2)–Fe(2)–C(2–3)	98.4 (4)
Fe(1)–N(1)–Fe(2)	82.1 (2)	Fe(1)–N(2)–Fe(2)	81.7 (2)
Fe(1)–N(1)–N(2)	68.9 (3)	Fe(1)–N(2)–N(1)	68.2 (3)
Fe(1)–N(1)–RC(7)	140.7 (5)	Fe(1)–N(2)–RC(1)	139.9 (4)
Fe(2)–N(1)–N(2)	68.8 (3)	Fe(2)–N(2)–N(1)	68.4 (3)
Fe(2)–N(1)–RC(7)	137.2 (5)	Fe(2)–N(2)–RC(1)	138.4 (4)
N(2)–N(1)–RC(7)	120.5 (5)	N(1)–N(2)–RC(1)	120.5 (5)
N(1)–RC(7)–RC(8)	116.5 (6)	N(2)–RC(1)–RC(2)	117.5 (6)
N(1)–RC(7)–RC(12)	119.6 (6)	N(2)–RC(1)–RC(6)	119.6 (6)
RC(8)–RC(7)–RC(12)	123.9 (7)	RC(2)–RC(1)–RC(6)	122.9 (6)
RC(7)–RC(8)–RC(9)	116.3 (8)	RC(1)–RC(2)–RC(3)	118.0 (7)
RC(8)–RC(9)–RC(10)	121.4 (10)	RC(2)–RC(3)–RC(4)	120.6 (8)
RC(9)–RC(10)–RC(11)	122.2 (10)	RC(3)–RC(4)–RC(5)	121.2 (9)
RC(10)–RC(11)–RC(12)	119.5 (8)	RC(4)–RC(5)–RC(6)	120.5 (8)
RC(7)–RC(12)–RC(11)	116.6 (7)	RC(1)–RC(6)–RC(5)	116.9 (6)
RC(6)–RC(12)–RC(7)	119.1 (6)	RC(1)–RC(6)–RC(12)	120.1 (6)
RC(6)–RC(12)–RC(11)	124.2 (7)	RC(5)–RC(6)–RC(12)	123.0 (6)
Fe(1)–C(1–1)–O(1–1)	177.4 (8)	Fe(2)–C(2–1)–O(2–1)	178.3 (7)
Fe(1)–C(1–2)–O(1–2)	177.8 (9)	Fe(2)–C(2–2)–O(2–2)	178.4 (8)
Fe(1)–C(1–3)–O(1–3)	177.3 (8)	Fe(2)–C(2–3)–O(2–3)	179.4 (8)

Cromer's values[15] of $\Delta f'$ and $\Delta f''$ were employed in evaluation of the contribution of the anomalous scattering of the iron atoms to the calculated structure factors. Programs utilized in this structural determination included the cell refinement and diffractometer setting program PICK2 by J. A. Ibers, the data processing program PICKOUT by R. J. Doedens and J. A. Ibers, Hamilton's GONO9 absorption correction program, the full-matrix least-squares program UCILS2

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(14) (a) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

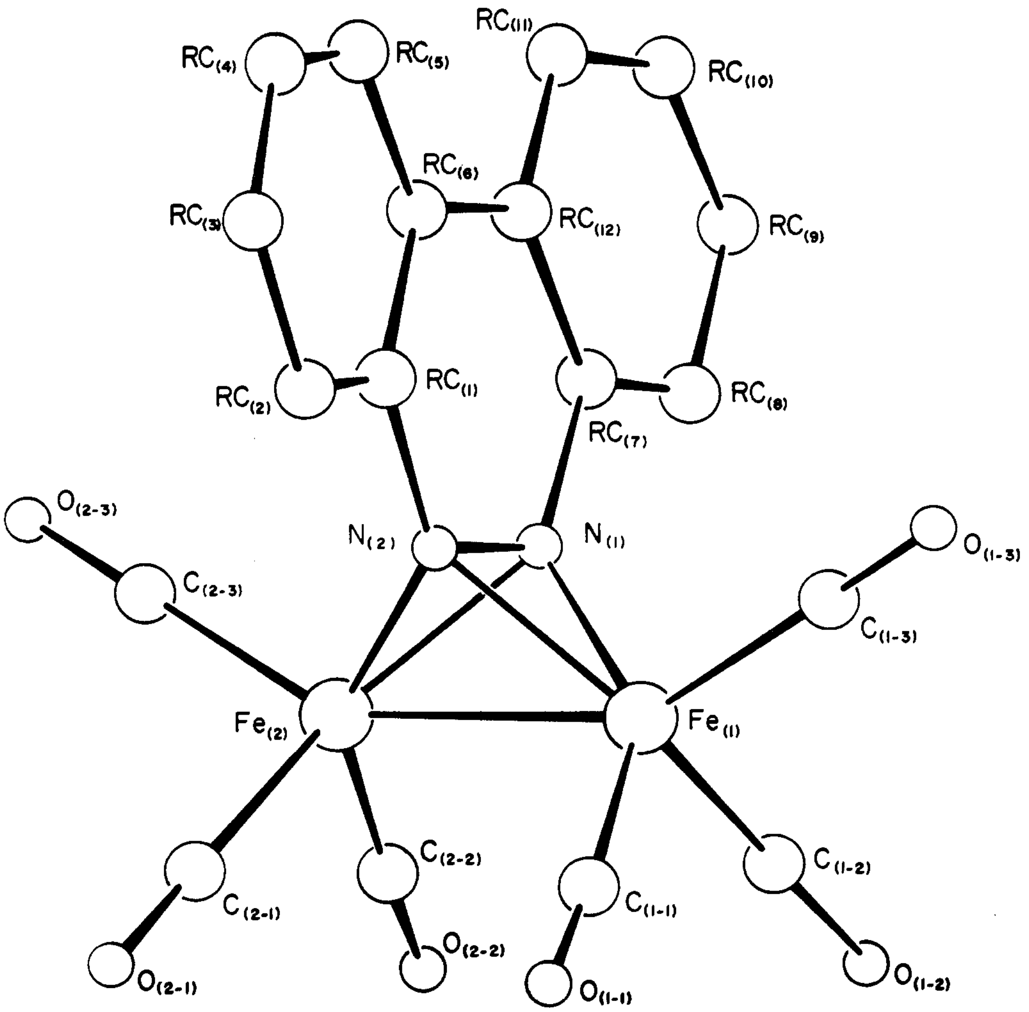

Figure 1.—A perspective view of the molecular structure of $C_{12}H_8N_2Fe_2(CO)_6$.

(derived from the Busing–Martin–Levy program ORFLS), modified versions of Zalkin's FORDAP Fourier summation program and the Busing–Martin–Levy function and error program ORFFE, and the figure-plotting program DANFIG by R. J. Dellaca and W. T. Robinson.

The observed and calculated structure factors (not including data with $F_o^2 < 3\sigma(F_o^2)$) are listed in Table I. Final atomic positional and thermal parameters are tabulated in Table II, and intramolecular distances and angles are given in Tables III and IV, respectively.

Description of the Structure

The binuclear benzo[*c*]cinnolinebis(tricarbonyliron) molecule contains two $Fe(CO)_3$ groups linked by two Fe–N–Fe bridges through the nitrogen atoms of the benzo[*c*]cinnoline molecule and also by an iron–iron bond of length 2.508 (4) Å. The resulting molecular configuration is depicted in Figure 1. Though no crystallographic symmetry is imposed upon the molecule, it possesses C_s-m symmetry within experimental error and deviates by a small but significant amount (*vide infra*) from C_{2v}-2mm symmetry. The presence of a nitrogen–nitrogen bond in the complex is clearly demonstrated by the N–N distance of 1.399 (8) Å; the overall molecular configuration is thus that proposed by Bennett.[10]

In Table V, selected bond lengths and angles of $C_{12}H_8N_2Fe_2(CO)_6$ are compared with those of other compounds which contain two $Fe(CO)_3$ groups doubly bridged by tetravalent nitrogen atoms. It is clear from the results tabulated that the iron–iron and iron–nitrogen distances in these compounds fall into two distinct groups, based upon the presence or absence of a direct nitrogen–nitrogen bond. In $C_{12}H_8N_2Fe_2(CO)_6$ and $[CH_3NFe(CO)_3]_2$, each of which contains a N–N bond, the Fe–Fe distances are longer by *ca.* 0.1 Å and the Fe–N distances are shorter by a comparable amount than the corresponding values for the other compounds listed. Thus the trends first noted[2] in $[CH_3NFe(CO)_3]_2$ are paralleled in the present case. The observed N–N bond length of 1.399 (8) Å is longer by a marginally significant amount than the corresponding distance of 1.366 (8) Å in $[CH_3NFe(CO)_3]_2$. The longer value is equal to twice the generally accepted single-bond covalent radius of a nitrogen atom,[16] and

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(16) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 221–230; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 106.

TABLE V

COMPARISON OF MOLECULAR PARAMETERS OF BINUCLEAR NITROGEN-BRIDGED IRON CARBONYLS[a]

(BOND LENGTHS IN Å AND ANGLES IN DEG)

	Ref	Fe–Fe	Fe–N	N–N	Fe–N–Fe	N–Fe–N	b
$(HNC_6H_4NC_6H_5)Fe_2(CO)_6$	4	2.372 (2)	2.00 (1)	2.38	72.5 (4)	72.9 (4)	95.4
$[(CH_3C_6H_4)_2CNNH]_2Fe_2(CO)_6$	5	2.40	2.00	c	c	c	c
$[(C_6H_5N)_2CO]Fe_2(CO)_6$	6, 7	2.409 (3)	2.00 (1)	2.15	74.5 (3)	65.0 (3)	92.4
$[H_2NFe(CO)_3]_2$	8	2.402 (6)	1.98 (2)	2.50 (3)	74.4 (7)	77.8 (8)	101.9 (8)
$[(CH_3N)_2CO]Fe_2(CO)_6$	9	2.391 (7)	1.97 (1)	2.10 (2)	75.0 (7)	64.8 (7)	92.2 (8)
$[CH_3NFe(CO)_3]_2$	2	2.496 (3)	1.878 (4)	1.366 (8)	83.4 (2)	42.7 (2)	91.1 (2)
$(C_{12}H_8N_2)Fe_2(CO)_6$	This work	2.508 (4)	1.914 (6)	1.399 (8)	81.9 (2)	42.9 (2)	89.5 (2)

[a] Where more than one chemically equivalent distance or angle is reported, an average value is tabulated with the standard deviation of an individual result. [b] Dihedral angle between the two Fe–N–N planes. [c] Not available.

the N–N bonds in both compounds can be regarded as single bonds. The coordination geometries about the iron atoms in these two compounds are also identical; the comments previously made[2] concerning the bonding in $[CH_3NFe(CO)_3]_2$ thus apply to the present compound as well.

A significant distortion of the benzo[*c*]cinnoline ligand from planarity reduces the overall molecular symmetry from C_{2v}-2mm to C_s-m. This distortion is clearly evident in Figure 2, a schematic diagram of the molecular structure as viewed down the direction defined by the N–N and Fe–Fe midpoints. Least-squares plane calculations, the results of which are summarized in Table VI, show that the two C_6 rings are planar and that the nonplanarity of the fused-ring system may be considered to result from a twisting of these two rings about the directions of the N–C bonds. This twisting is the means by which the ligand accommodates to the difference of 0.06 Å between the lengths of the RC(6)–RC(12) and N(1)–N(2) bonds in the central ring. No structural information is available for benzo[*c*]cinnoline itself, though its three rings have commonly been assumed to be coplanar.[17,18]

TABLE VI

LEAST-SQUARES PLANES FOR THE BENZO[*c*]CINNOLINE LIGAND[a]

1. Plane Containing N(1), N(2), and RC(1)–RC(12). Equation of Plane:[b] $-0.8721X + 0.4753Y - 0.1165Z = -3.0768$

Distances of atoms to plane, Å

N(1)	0.057	RC(5)	0.051	RC(11)	0.088
N(2)	0.081	RC(6)	0.062	RC(12)	0.069
RC(1)	0.016	RC(7)	−0.007	Fe(1)	−1.083
RC(2)	−0.075	RC(8)	−0.088	Fe(2)	1.419
RC(3)	−0.100	RC(9)	−0.110		
RC(4)	−0.034	RC(10)	−0.012		

2. Plane Containing RC(1)–RC(6). Equation of Plane:. $-0.8401X + 0.5275Y - 0.1264Z = -3.0099$

Distances of atoms to plane, Å

RC(1)	0.007	RC(4)	0.002	Fe(1)	−1.127
RC(2)	0.000	RC(5)	0.005	Fe(2)	1.364
RC(3)	−0.004	RC(6)	−0.009		

3. Plane Containing RC(7)–RC(12). Equation of Plane: $-0.8950X + 0.4428Y - 0.0534Z = -3.2432$

Distances of atoms to plane, Å

RC(7)	0.001	RC(10)	0.001	Fe(1)	−1.063
RC(8)	0.011	RC(11)	0.011	Fe(2)	1.427
RC(9)	−0.013	RC(12)	−0.012		

4. Plane Containing N(1), N(2), RC(1), RC(6), RC(7), RC(12). Equation of Plane: $-0.8757X + 0.4691Y - 0.1146Z = -3.0302$

Distances of atoms to plane, Å

N(1)	0.014	RC(6)	0.012	Fe(1)	−1.133
N(2)	0.028	RC(7)	−0.043	Fe(2)	1.370
RC(1)	−0.041	RC(12)	0.030		

[a] Unit weights were employed in the calculation of all planes. [b] The equations of the planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal coordinate system (*A*, *B*, *C*) oriented with respect to the crystallographic (*a*, *b*, *c*) axes such that *A* is parallel to *a* and *B* lies in the (*a*, *b*) plane.

The root-mean-square deviation of the 12 observed individual C–C distances in the two C_6 rings from their mean value of 1.384 Å is 0.019 Å. Since these bond-length variations form no consistent pattern, it is likely that the standard deviations of the ring C–C distances are underestimated by a factor of about 1.5. A full anisotropic refinement might have improved this situation, but was not judged to be a worthwhile investment of computer time. The RC(6)–RC(12) distance of 1.462 (10) Å is only slightly less than the value of 1.48 Å proposed[19,20] for a single bond between two trigonally hybridized carbon atoms. The N(1)–RC(7) and N(2)–RC(1) distances of 1.419 (9) and 1.410 (8) Å are likewise reasonable values. None of the interior angles of the C_4N_2 ring differs significantly from 120°. Small but apparently significant variations are however observed in the interior angles of the two C_6 rings. These angles range from 116.3 (8) to 123.9 (6)°, with the same pattern of variation being exhibited by the angles in both rings.

The configurations of the carbonyl groups are as expected, with mean Fe–C and C–O distances of 1.768 (4) Å and 1.159 (4) Å, respectively. None of the Fe–C–O angles is significantly nonlinear. Nonbonded intermolecular contacts are normal for this type of crystal, with the shortest of various types being: H · · · H, 2.39 Å; O · · · H, 2.55 Å; C · · · H, 3.10 Å; O · · · O, 3.04 Å; C · · · C, 3.39 Å; C · · · O, 3.42 Å. The principal rms amplitudes of thermal motion of the iron atoms (0.184 (2), 0.232 (2), and 0.249 (2) Å for Fe(1); 0.192 (2), 0.226 (2), and 0.237 (2) Å for Fe(2)) are reasonable as are the trends in the isotropic thermal parameters of the light atoms.

Discussion

At first sight it is difficult to understand the marked difference in iron–iron and iron–nitrogen bond lengths between the first five compounds listed in Table V

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(17) P. F. Holt and A. N. Hughes, *J. Chem. Soc.*, 3216 (1960).

(18) K. E. Buage and J. W. Smith, *ibid.*, 5292 (1962).

(19) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(20) D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, **A258**, 270 (1960).

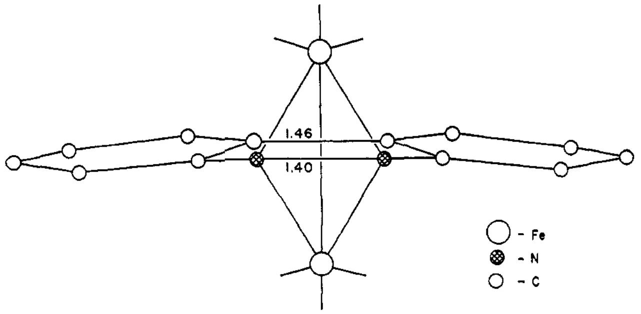

Figure 2.—Schematic diagram of the $C_{12}H_8N_2Fe_2(CO)_6$ molecule, as viewed down the direction defined by the N–N and Fe–Fe midpoints. The dihedral angle between the planes of the two C_6 rings is 7.2°.

and the last two. In view of the small variations in Fe–Fe and Fe–N bond lengths within each of these groups, it seems likely that the differences are a stereochemical consequence of the presence of a N–N bond in the latter two compounds and do not have their origin in any more subtle electronic property of the bridging ligands. It has already been suggested[2] that a qualitative valence-bond description involving hexacoordinate metal atoms and iron–nitrogen σ bonds of formal unit order is an appropriate first approximation for description of the bonding in all of these compounds. This conclusion was also reached for the sulfur-bridged dimers $[SFe(CO)_3]_2$[21] and $[C_2H_5SFe(CO)_3]_2$,[22] which are electronically and structurally analogous to $[CH_3NFe(CO)_3]_2$ and $[H_2NFe(CO)_3]_2$, respectively. The sulfur compounds do not, however, exhibit a variation in bond lengths nearly as great as that found in the nitrogen systems (for $[SFe(CO)_3]_2$, Fe–Fe = 2.552 (2) Å, mean Fe–S = 2.228 (2) Å; for $[C_2H_5SFe(CO)_3]_2$, Fe–Fe = 2.537 (10) Å, mean Fe–S = 2.259 (7) Å). The differences in the Fe–Fe and Fe–S distances are in the same directions as the comparable differences in the nitrogen compounds but of a much smaller magnitude. As has previously been noted,[2,23] a correlation exists in both the N- and S-bridged series between the Fe–Fe and Fe–N (or Fe–S) bond lengths, with a longer metal–metal bond associated in general with a shorter bond to the bridging atom. This effect is much more apparent in the nitrogen-bridged series, and the observed variation in the lengths of formal single bonds serves as another example of the limitation of the concept of single-bond covalent radii when applied to bonds involving metal atoms, even in a series of closely similar compounds.

A structural parameter of some interest for the nitrogen-bridged iron carbonyls is the dihedral angle between the two Fe–N–N planes. Values of this angle are tabulated in the last column of Table V. For given Fe–Fe and Fe–N distances, the value of this dihedral angle will depend upon the nitrogen–nitrogen distance, asymptotically approaching a lower limit equal to the Fe–N–Fe angle as the N–N distance becomes very small. The form of this variation is illustrated in Figure 3 by the solid line, calculated on the basis of typical Fe–Fe and Fe–N distances found in compounds not containing an N–N bond. Substantial deviations from the calculated values are observed whenever the N–N distance is such that the calculated dihedral angle is less than 90°. Among the compounds studied to date, this is true only for those which contain an N–N bond, *i.e.*, for $[CH_3NFe(CO)_3]_2$ and $C_{12}H_8N_2Fe_2(CO)_6$. In each of these compounds, the angle in question is maintained near 90° by an increase in the Fe–Fe bond length.

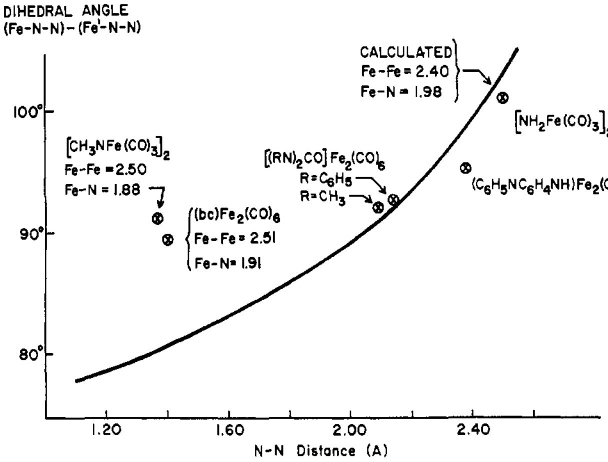

Figure 3.—Plot of dihedral angle between the two Fe–N–N planes *vs.* N–N distance for N-bridged iron carbonyl dimers. The abbreviation bc denotes benzo[*c*]cinnoline. Data are taken from ref 2, 4–9, and this work.

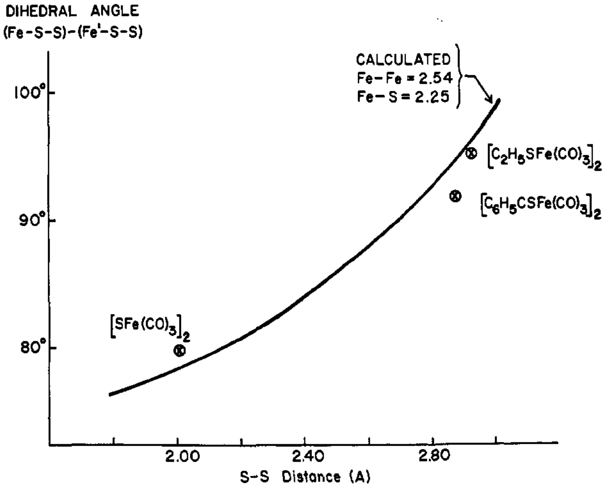

Figure 4.—Plot of dihedral angle between the two Fe–S–S planes *vs.* S–S distance for S-bridged iron carbonyl dimers. Data are taken from ref 21–23.

A comparable plot of dihedral angle *vs.* S–S distance for sulfur-bridged iron carbonyl dimers of known structure is shown in Figure 4. In these compounds, little variation in Fe–Fe and Fe–S distances exists, and the observed dihedral angles all fall close to a single calculated curve. The smallest of the observed angles is 79.8 (5)°, nearly 10° less than the minimum value in the nitrogen-bridged systems.

The difference between the observed structural trends in the nitrogen and sulfur-bridged dimers may thus be simply and plausibly rationalized as stemming

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(21) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(22) L. F. Dahl and C. H. Wei, *ibid.*, **2**, 328 (1963).

(23) H. P. Weber and R. F. Bryan, *J. Chem. Soc., A*, 182 (1967).

from the resistance of the bridging nitrogen atoms to large deformations from a tetrahedral configuration. For compounds which contain an N–N bond, the dihedral angle defined above may provide a means of estimating the limits of deformation of the bridging system. Further structural studies on related compounds are being carried out to determine whether this approach is one of general predictive utility.

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The Crystal and Molecular Structure of Trifluorosilyltetracarbonylcobalt

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The crystal and molecular structure of trifluorosilyltetracarbonyl cobalt, $Co(SiF_3)(CO)_4$, has been determined from three-dimensional X-ray photographic data. The structure has been solved by symbolic addition and refined by least-squares procedures. The R factor for 375 intensities above background is 7.7%. The material crystallizes in space group Cmca of the orthorhombic system with eight molecules in a cell of dimensions $a = 8.224$ (4), $b = 11.418$ (10), and $c = 18.591$ (7) Å. The Co–Si distance is very slightly shorter than that of the chloro derivative, but there are no other significant differences between the structures of the two molecules.

Introduction

In recent years there has been widespread interest in complexes of nonmetallic second-row donor elements with transition metals and, in particular, the role of (d → d) π bonding in stabilizing such complexes.[1–3] Few comparative data bearing on this question have been available. Recently Robinson and Ibers[1] determined the structure of $Cl_3SiCo(CO)_4$ by X-ray diffraction; the structure of $H_3SiCo(CO)_4$ has been studied by electron diffraction methods.[2] This paper reports the X-ray determination of the structure of a third member of this series, $(F_3Si)Co(CO)_4$. Earlier spectral work indicated that all three molecules had the same basic trigonal-bipyramidal structure, and hence it seemed likely that a comparison of bond lengths in the three compounds would be very useful in assessing the importance of (d → d) π bonding.

Experimental Section

Preparation of Crystals.—A sample of $Co(SiF_3)(CO)_4$, prepared by procedures first outlined by Chalk and Harrod,[4] was kindly supplied by Dr. A. P. Hagen. Crystals were grown by subliming the sample from a break-seal tube into a glass capillary through which the vapor was drawn by a vacuum pump; the capillary was designed so that it could be immersed in liquid nitrogen and easily sealed and removed.

Computations.—Calculations were carried out on an IBM 360/44 computer with 16 K words of core storage and twin 2315-disk drives. The programs used have been footnoted in the text.

Determination of Space Group and Unit Cell Dimensions.—The melting point of the compound is 18°, and therefore capillaries containing the crystals were stored, handled, and photographed in a refrigerated room at temperatures between 0 and 6°. Several different pale yellow transparent crystals were mounted and examined. Only one crystal form was found. Precession and Weissenberg photographs in several different orientations showed that the diffraction symmetry was mmm with extinctions $h + k$ odd for hkl, l odd for $h0l$, and h odd for $hk0$. These absences are consistent with space group Cmca or (with a permutation of axes) Aba2. After the complete set of structure factors had been collected and scaled (*vide infra*), normalized structure factors[5] were calculated using the program SHNORM.[6] The distribution of normalized structure factors was compared with the theoretical distributions for centric and acentric structures;[7] the observed distribution was very close to the theoretical centric distribution. The space group Cmca was therefore chosen for refinement.

Data for unit cell determination were taken from a crystal mounted with the [110] axis parallel to the goniometer axis. Precession photographs of the $hk0$ and hhl zones were taken with Co Kα radiation. All distances greater than 9.0 cm between equivalent spots were measured using a cathetometer which could be read to 0.002 mm. These distances together with the reflection indices were used as input to program CELGLS which uses an iterative least-squares procedure to refine the cell parameters. These were $a = 8.224$ (4), $b = 11.418$ (10), and $c = 18.591$ (7) Å.

Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant digits and are usually derived from the inverse matrix in nonlinear least-squares calculations.

Film shrinkage corrections were not made because the photographs had been collected at one temperature and developed at another. The spots were not especially sharp and the magnitude

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(1) W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

(2) A. G. Robiette, G. M. Sheldinck, R. N. F. Simpson, B. J. Aylett, and J. A. Campbell, *J. Organometal. Chem.* (Amsterdam), **14**, 279 (1968).

(3) A. P. Hagen and A. G. McDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

(4) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

(5) H. Hauptmann and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Pittsburgh, Pa., 1953.

(6) SHNORM is a program derived from NRC-4 (S. R. Hall and F. R. Ahmed) to calculate normalized structure factors.

(7) I. L. Karle, K. Britts, and P. Gum, *Acta Cryst.*, **17**, 496 (1964).