both a tetrahedral $Re_4(CO)_{16}$ molecule and a square-planar $Re_4(CO)_{16}^{4-}$ anion, each metal atom would attain the appropriate noble gas configuration. It might be possible, therefore, for the known $Re_4(CO)_{16}^{2-}$ ion to undergo both a two-electron oxidation (to the tetrahedral neutral species) and a two-electron reduction (to the square-planar tetraanion). Experiments involving these and related reactions are presently in progress in the laboratories of Professor H. D. Kaesz.

The Tetra-*n*-butylammonium Cation

The over-all configuration of the tetra-*n*-butylammonium cation is shown in Figure 1. Three of the *n*-butyl limbs take up a *trans* conformation, while the fourth limb has a *gauche* conformation in which the terminal two carbon atoms may reasonably be assumed to be disordered. A survey of the thermal parameters of the carbon atoms within the tetra-*n*-butylammonium ion shows evidence of large amplitudes of thermal motion. [Mean isotropic thermal parameters are 7.0 Å^2 for α-carbon atoms, 9.1 Å^2 for β-carbons, 9.0 Å^2 for γ-carbons (neglecting C_{19}), and 12.8 Å^2 for δ-carbons (neglecting C_{20}).]

It should be emphasized that disorder of the terminal $-CH_2-CH_3$ group of a single *n*-butyl group has previously been reported for $[(n\text{-}C_4H_9)_4N]_2[Fe_2(S_2C_2(CN)_2)_4]$,[40] and disorder of a single terminal methyl group probably occurs in $[(n\text{-}C_4H_9)_4N][Cu(S_2C_2(CN)_2)]$.[41] Similarly, although the $(n\text{-}C_4H_9)_4N^+$ ion in $[(n\text{-}C_4H_9)_4N][Co(S_2C_2(CN)_2)_2]$[42] is ordered, even here three of the *n*-butyl chains adopt the *trans* conformation while the fourth takes up a *gauche* conformation.

These observations should result in some hesitation in using tetra-*n*-butylammonium salts in future crystallographic investigations.

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Crystal Structure and Absolute Configuration of (−)-Tetracarbonyl(fumaric acid)iron

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The molecular and crystal structure of (−)-tetracarbonyl(fumaric acid)iron ((−)-$Fe(CO)_4(CHCOOH)_2$) has been determined by X-ray diffraction methods. The unit cell of $P2_12_12$ symmetry (a = 6.10 (2) Å, b = 13.37 (4) Å, c = 19.20 (6) Å) contains six molecules of the $Fe(CO)_4(CHCOOH)_2$ formula. The measured and calculated densities are, respectively, 1.77 and 1.80 g cm^{-3}. A total of 610 nonzero intensities were collected photographically by Weissenberg equiinclination methods. The structure was determined by the Patterson method and refined by the least-squares method to a conventional R factor of 11.6%. A trigonal-bipyramidal coordination of the ligands around the central iron atom has been found. Two significantly different conformations are observed of the same molecule since only one of the three crystallographically independent molecules shows the C=C group of the coordinated fumaric acid lying on the equatorial plane. For two molecules, on the contrary, a significant deviation from the planarity is observed. The absolute configuration has been determined utilizing the anomalous diffraction of the Cu Kα radiation by the iron atom. According to the rule used by Cahn, Ingold, and Prelog the absolute configuration is R,R. Two different patterns of hydrogen bonding have been observed. Each molecule of type A is hydrogen bonded to four others of the same type. Molecules of type B and C, on the other hand, are hydrogen bonded according to the sequence... B–C–B–C....

Introduction

Recent studies on olefin and transition metal complexes carried out in our laboratory have shown that when an olefinic compound without asymmetric substituents and with no symmetry plane normal to the plane of the double bond is π bonded to a coordinative center, pairs of enantiomorphic molecules are obtained.[1–8] The structures of some of these complexes containing Pt or Fe as the coordination center are under study in our laboratory. In this paper we report the results of a three-dimensional X-ray study on the (−)-$Fe(CO)_4(CHCOOH)_2$ complex.

Experimental Section

A sample of racemic tetracarbonyl(fumaric acid)iron, $Fe(CO)_4(CHCOOH)_2$, was prepared following the method described by

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[1] G. Paiaro, P. Corradini, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, **71**, 184 (1964).

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Weiss, et al.[9] The resolution of the two enantiomers was obtained by crystallization of the corresponding brucine salts.

The optical activity of the (−) form was: $[\alpha]^{25}\text{D}$ −578° (in acetone). Crystals suitable for X-ray study were obtained by slow evaporation of a solution of the compound in aqueous hydrochloric acid.

The unit cell parameters were obtained from Weissenberg photographs (Fe Kα): a = 6.10 (2) Å, b = 13.37 (4) Å, c = 19.20 (6) Å, Z = 6, d_{exptl} = 1.77 (2) g cm^{-3}, and d_{calcd} = 1.80 g cm^{-3}. (In parentheses are reported the standard deviations in the last digits.)

Space group $P2_12_12$ was uniquely determined from the analysis of the systematic absences. Three-dimensional intensity data were collected photographically by use of the Weissenberg equiinclination method and Fe Kα radiation. The crystal used for collecting most of the data (levels $hk0$–$hk9$) was a prism of dimensions 0.15 × 0.2 × 0.5 mm, the 0.5-mm direction being parallel to the c axis. Further data ($h0l$–$h2l$) were collected using a crystal of dimensions 0.2 × 0.2 × 0.5 mm.

The linear absorption coefficient is μ = 52.7 cm^{-1}. Assuming for the crystal an approximately cylindrical shape, a maximum difference of 10% in the absorption correction factor results. The intensities of 610 observed reflections visually estimated were put on a common scale according to the method of Rollet and Sparks.[10] No absorption correction was applied. The values given by Hanson, *et al.*,[11] for the scattering factors were used.

A correction of −1.4 e$^-$ was applied to take into account the real contribution of the anomalous diffraction. This value for the correction had been found empirically satisfactory during the refinement of the structure of the racemic form.[12]

Determination and Refinement of the Structure

The presence of six molecules in a unit cell of $P2_12_12$ symmetry suggested that, in analogy with the structure of the racemic form of the same compound, the molecules were situated along the twofold crystallographic axis with the iron atoms in special positions on the symmetry axis. In fact, while the lengths of the a and b axes of the two forms are nearly equal, that of the c axis of the (−) form is three-halves that of the racemic one. Strong analogies were found between the distributions of the intensities of the $0kl$ reflections for the two forms. The structure was solved by interpretation of the three-dimensional Patterson synthesis. The structure of the racemic form, which had been already solved, was of great help in the interpretation of the Patterson function of the optically active compound. The iron atoms were easily located. The general orientation of the three independent molecules around the twofold axis was found jointly by the accurate analysis of the Patterson peak distribution within 3 Å from the origin and by analysis of the packing of the resulting possible models.

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	B, Å^2
C(1A)	−0.1416 (61)	0.6188 (26)	0.1406 (19)	4.58 (81)
C(2A)	0.1116 (59)	0.5116 (33)	0.0352 (16)	4.61 (79)
C(3A)	0.1633 (55)	0.6179 (23)	0.0195 (16)	3.41 (73)
C(4A)	0.2131 (59)	0.5538 (27)	0.1947 (18)	3.89 (72)
O(1A)	−0.2416 (42)	0.6911 (19)	0.1417 (14)	5.67 (62)
O(2A)	0.0339 (41)	0.6844 (16)	0.0090 (11)	4.30 (49)
O(3A)	0.3736 (39)	0.6328 (17)	0.0170 (11)	4.26 (51)
O(4A)	0.3406 (49)	0.5959 (21)	0.2232 (14)	6.02 (65)
Fe(A)	0.0	0.5	0.1379 (4)	...
C(1B)	0.3631 (64)	0.6227 (27)	0.4825 (19)	4.79 (87)
C(2B)	−0.3956 (50)	0.5079 (29)	0.3790 (14)	3.45 (64)
C(3B)	−0.3022 (59)	0.6107 (24)	0.3633 (18)	4.02 (74)
C(4B)	0.7304 (55)	0.5523 (25)	0.5314 (16)	3.35 (69)
O(1B)	0.2785 (45)	0.6934 (19)	0.4910 (14)	5.38 (60)
O(2B)	−0.4368 (35)	0.6843 (16)	0.3630 (11)	3.98 (47)
O(3B)	−0.0994 (39)	0.6180 (17)	0.3490 (12)	4.53 (52)
O(4B)	0.8579 (45)	0.5911 (18)	0.5624 (12)	4.95 (58)
Fe(B)	0.5	0.5	0.4809 (4)	...
C(1C)	−0.7538 (66)	0.5681 (31)	0.8116 (20)	5.23 (92)
C(2C)	0.5614 (50)	0.5442 (23)	0.7051 (15)	3.22 (68)
C(3C)	0.4605 (60)	0.6438 (25)	0.6833 (17)	4.10 (76)
C(4C)	0.6136 (67)	0.5977 (28)	0.8592 (20)	5.22 (86)
O(1C)	0.0868 (49)	0.6081 (22)	0.8098 (15)	6.88 (73)
O(2C)	0.2652 (44)	0.6417 (22)	0.6699 (13)	5.71 (64)
O(3C)	0.5991 (45)	0.7165 (20)	0.6867 (13)	5.75 (64)
O(4C)	0.6906 (51)	0.6631 (23)	0.8887 (13)	7.13 (77)
Fe(C)	0.5	0.5	0.8045 (4)	...

Anisotropic Thermal Parameters of the Iron Atoms

Atom	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Fe(A)	4.34 (37)	1.06 (37)	...	2.71 (29)	...	4.71 (38)
Fe(B)	3.31 (43)	−1.03 (35)	...	2.04 (28)	...	5.44 (43)
Fe(C)	3.93 (37)	−0.74 (42)	...	3.59 (33)	...	5.46 (42)

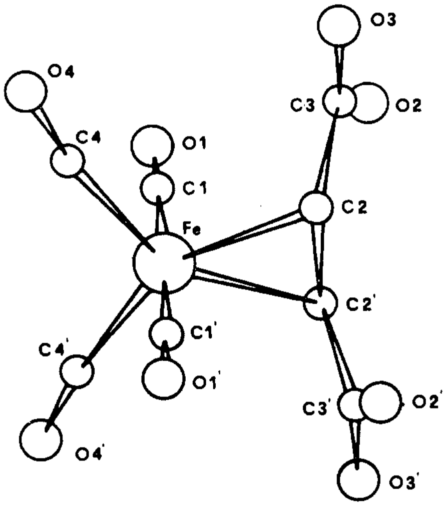

Figure 1.—Molecular model of (−)-Fe(CO)$_4$(CHCOOH)$_2$.

In particular, it was possible with this method to define the orientation of the apical carbonyls of the three independent molecules and, consequently, to build up a first consistent model of the crystal structure. An R factor ($\Sigma|\Delta F|/\Sigma|F_o|$) of 33% was the result of the first structure factor calculation, which was considered a sufficiently good demonstration of the over-all correctness of the structure. The refinement was initially carried out for the centrosymmetric (100) projection by successive Fourier and difference Fourier synthesis calculations. The coordinates obtained in this way (the x coordinate was determined from stereochemical considerations) were used as a starting point for the final three-dimensional refinement. This was carried out by the block-diagonal-matrix least-squares method. The minimized function was $R_w = \Sigma_{hkl}w(\Delta F)^2/\Sigma_{hkl}|F_o|^2$. Thermal parameters were allowed to vary isotropically at the first stages up to a conventional R factor of 15%. The refinement was than continued

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Table II

Comparison between Observed and Calculated Structure Factors ($F(000) = 828$)

h	k	F_o	F_c
l=0			
2	0	46	43
4	0	27	36
6	0	14	12
1	1	71	71
2	1	9	7
3	1	25	22
4	1	25	21
5	1	26	18
6	1	9	10
0	2	128	155
1	2	16	13
2	2	85	93
3	2	22	18
4	2	45	38
6	2	19	23
1	3	19	17
2	3	41	38
3	3	55	54
6	3	12	13
0	4	48	43
1	4	18	14
2	4	123	119
3	4	13	12
4	4	92	71
1	5	75	65
2	5	47	36
0	6	107	108
1	6	33	29
2	6	102	91
3	6	27	24
4	6	62	58
1	7	32	29
2	7	53	42
3	7	21	17
4	7	17	12
0	8	75	80
2	8	77	71
5	8	12	8
2	9	10	6
3	9	19	15
4	9	15	10
0	10	85	82
2	10	55	50
4	10	13	14
0	12	13	23
1	12	14	12
2	12	38	38
1	13	17	15
2	13	11	8
l=1			
1	0	81	106
2	0	15	11
3	0	44	41
5	0	27	20
1	1	101	106
2	1	30	32
3	1	37	36
4	1	21	17
5	1	33	28
1	2	61	62
2	2	62	56
3	2	75	69
5	2	23	22
1	3	41	37
2	3	39	33
3	3	18	17
0	4	23	20
1	4	97	97
2	4	15	15
3	4	53	52
4	4	18	21
5	4	24	20
1	5	121	108
2	5	12	11
3	5	40	34
0	5	23	18
1	6	54	48
2	6	16	13
3	6	28	23
5	6	23	25
1	7	40	39
2	7	23	19
3	7	29	22
4	7	18	18
1	8	49	40
2	8	28	19
3	8	36	29
0	9	18	15
1	9	35	29
2	9	17	12
1	10	17	14
2	10	16	13
3	10	26	21
0	11	30	19
1	11	35	30
2	11	8	5
3	11	26	22
2	12	8	6
3	12	13	19
0	13	16	10
l=2			
0	0	19	17
1	0	107	106
3	0	10	12
5	0	33	30
1	1	32	28
2	1	32	32
3	1	15	12
4	1	12	12
0	2	18	20
1	2	95	88
2	2	66	61
3	2	50	44
4	2	14	14
5	2	19	17
1	3	37	36
2	3	27	22
3	3	36	30
4	3	14	10
5	3	20	17
1	4	125	106
3	4	66	59
4	4	17	16
5	4	12	14
0	5	27	19
1	5	58	46
3	5	12	11
5	5	18	20
0	6	49	45
1	6	80	73
2	6	24	20
3	6	44	39
5	6	18	17
0	7	13	11
1	7	33	29
2	7	13	9
3	7	23	13
4	7	15	12
1	8	31	31
3	8	26	24
4	8	15	14
1	9	36	24
3	9	20	23
0	10	22	15
1	10	57	48
3	10	20	20
0	11	23	17
3	11	14	14
1	12	42	35
2	12	18	16
l=3			
0	0	57	82
1	0	27	28
2	0	16	17
3	0	20	22
4	0	62	67
6	0	16	23
0	1	87	96
1	1	18	19
2	1	78	82
3	1	21	21
4	1	22	21
5	1	12	15
0	2	121	148
1	2	19	19
2	2	119	108
3	2	16	15
4	2	46	51
0	3	33	35
1	3	53	47
2	3	48	51
3	3	29	24
4	3	24	24
6	3	10	12
0	4	95	97
1	4	48	38
2	4	66	59
3	4	16	16
4	4	56	64
0	5	92	88
1	5	27	26
2	5	46	43
3	5	24	25
4	5	19	18
1	6	37	30
2	6	45	47
3	6	14	13
4	6	43	45
5	6	14	5
0	7	72	59
1	7	27	23
2	7	37	32
3	7	18	21
4	7	33	27
0	8	15	22
1	8	29	25
2	8	118	96
4	8	23	27
0	9	48	44
1	9	18	19
2	9	25	21
3	9	12	14
0	10	54	51
2	10	32	38
4	10	18	24
0	11	17	16
1	11	24	26
2	11	23	19
3	11	11	11
0	12	36	40
2	12	36	32
l=4			
1	0	71	76
2	0	12	11
3	0	33	35
5	0	21	21
0	1	33	34
1	1	73	68
2	1	32	30
3	1	48	44
5	1	21	23
0	2	25	25
1	2	145	139
2	2	12	15
3	2	42	35
5	2	16	19
0	3	38	37
1	3	95	89
2	3	28	25
3	3	78	72
5	3	33	37
0	4	18	20
1	4	70	62
4	4	15	15
5	4	19	23
0	5	50	47
1	5	11	10
2	5	18	20
3	5	45	41
5	5	29	36
0	6	12	12
1	6	43	37
2	6	25	25
3	6	16	18
5	6	10	15
1	7	61	54
2	7	15	12
3	7	44	41
1	8	17	15
3	8	17	15
0	9	21	16
1	9	55	47
3	9	31	32
3	10	19	20
0	11	24	18
3	11	20	21
1	12	27	21
2	12	8	8
1	13	18	20
l=5			
0	0	19	18
1	0	91	93
2	0	12	15
4	0	20	21
5	0	13	13
0	1	19	14
1	1	105	102
3	1	15	15
0	2	56	59
1	2	73	76
2	2	54	54
3	2	54	49
5	2	18	19
0	3	18	18
1	3	92	87
3	3	20	15
5	3	11	12
0	4	27	31
1	4	42	34
2	4	20	20
3	4	63	56
4	4	14	13
5	4	27	31
1	5	28	24
2	5	15	13
4	5	13	15
0	6	33	32
1	6	16	15
2	6	29	28
3	6	34	36
4	6	14	12
0	7	17	15
1	7	27	23
2	7	15	15
5	7	17	14
1	8	54	50
2	8	27	20
3	8	38	28
1	9	11	10
0	10	15	12
1	10	24	24
2	10	12	9
3	10	14	17
0	11	14	11
1	11	16	16
1	12	10	15
2	12	8	7
0	13	9	9
1	13	6	7
l=6			
0	0	202	263
1	0	45	49
2	0	36	37
3	0	26	25
4	0	28	34
0	1	47	42
1	1	36	33
2	1	73	71
3	1	21	23
4	1	55	54
5	1	11	10
0	2	27	15
1	2	51	53
2	2	40	41
3	2	11	13
4	2	27	26
0	3	79	89
1	3	18	23
2	3	84	80
3	3	27	26
4	3	41	37
5	3	10	12
0	4	15	10
1	4	27	31
2	4	41	43
4	4	37	32
1	5	30	24
4	5	36	37
0	5	62	57
0	6	74	54
1	6	21	18
2	6	46	47
3	6	16	14
4	6	38	30
0	7	45	48
1	7	16	14
2	7	54	49
3	7	18	17
4	7	26	30
0	8	42	40
1	8	21	18
2	8	33	32
0	9	42	39
1	9	16	14
2	9	44	41
0	10	38	30
2	10	27	26
0	11	33	31
2	11	19	21
2	12	21	22
0	13	18	24
l=7			
0	0	19	17
1	0	34	31
4	0	12	14
0	1	27	33
1	1	87	80
3	1	30	32
4	1	11	14
5	1	30	32
0	2	26	26
1	2	41	44
3	2	32	27
4	2	14	16
0	3	20	15
1	3	42	43
3	3	48	44
5	3	12	13
1	4	26	20
3	4	40	39
5	4	12	15
1	5	89	81
3	5	71	60
4	5	11	10
5	5	12	16
1	6	31	20
2	6	12	12
3	6	12	11
0	7	15	17
1	7	44	42
2	7	10	9
3	7	34	33
4	7	8	12
0	8	15	11
1	8	17	15
2	8	12	14
3	8	9	11
1	9	33	35
3	9	11	15
1	10	9	10
2	10	11	12
3	10	7	9
1	11	47	45
3	11	14	19
l=8			
0	0	50	52
1	0	80	62
3	0	13	13
5	0	8	10
0	1	15	15
1	1	12	8
2	1	12	14
3	1	57	54
4	1	8	8
5	1	10	13
0	2	25	28
1	2	42	43
2	2	24	28
3	2	14	17
4	2	10	12
1	3	21	25
3	3	12	13
5	3	10	9
1	4	32	32
2	4	20	18
3	4	28	27
4	4	15	17
0	5	29	30
1	5	43	48
3	5	16	13
5	5	6	8
0	6	56	54
1	6	24	22
3	6	32	27
5	6	5	9
0	7	27	24
1	7	25	22
2	7	10	6
3	7	20	19
4	7	11	12
0	8	14	12
1	8	19	16
1	9	16	15
2	9	15	12
0	10	33	30
1	10	24	24
l=9			
0	0	45	49
1	0	31	29
3	0	29	21
5	0	7	11
0	1	135	166
1	1	23	24
2	1	69	74
3	1	12	11
4	1	28	20
0	2	31	29
2	2	26	28
3	2	21	21
1	3	22	23
2	3	75	75
4	3	30	30
0	4	58	64
1	4	32	34
2	4	10	11
3	4	11	10
0	5	66	65
1	5	15	16
2	5	68	59
3	5	18	21
4	5	33	38
0	6	18	13
1	6	33	33
2	6	20	25
3	6	17	16
4	6	19	21
0	7	72	66
2	7	48	43
3	7	14	15
4	7	15	19
2	8	18	14
3	8	10	13
0	9	59	64
2	9	25	23
0	11	26	34
1	11	10	13
2	11	19	20
l=10			
0	0	32	31
1	0	75	75
2	0	15	18
1	1	64	64
1	2	58	57
2	2	12	10
0	3	26	22
1	3	59	52
0	4	21	24
1	4	30	28
2	4	11	11
0	5	19	17
1	5	28	30
0	6	22	18
1	6	40	42
2	6	11	11
1	7	40	42
1	8	30	28
2	9	10	9
1	9	33	31
1	10	24	24
1	11	8	9
l=11			
0	0	19	14
0	1	26	21
1	1	38	42
2	1	12	16
1	2	10	11
2	2	34	38
1	3	44	45
2	3	11	12
0	4	20	18
2	4	11	13
1	5	36	39
2	5	11	15
0	6	21	15
0	7	20	14
1	7	27	26
0	8	18	19
1	8	19	21
2	8	14	15
0	9	21	15
1	9	15	14
0	11	8	9
1	11	10	13
l=12			
0	0	42	35
2	0	15	15
0	1	41	39
2	1	35	33
0	2	49	49
1	2	34	36
2	2	29	22
0	3	55	53
2	3	59	63
0	4	37	33
1	4	25	25
2	4	18	17
0	5	36	33
1	5	11	12
2	5	26	19
0	6	17	9
1	6	19	17
2	6	15	18
0	7	30	24
1	7	10	10
2	7	30	32
0	8	14	8
1	8	12	12
2	8	16	18
0	9	25	27
1	9	10	10
2	9	26	26
0	10	10	10
l=13			
0	0	15	14
1	0	24	22
1	1	13	22
0	2	17	17
1	2	40	44
2	2	10	13
1	4	32	27
2	4	12	11
1	5	23	27
1	6	27	27
1	8	27	29
2	8	8	11
1	10	6	11
l=14			
0	0	26	29
2	0	12	14
1	1	13	17
2	1	12	12
1	2	14	21
2	2	12	19
1	3	10	12
2	3	11	10
1	5	12	13
2	6	10	12
1	7	17	18
l=15			
0	0	20	19
2	0	13	11
0	1	40	50
2	1	17	13
0	2	21	23
2	2	20	19
0	3	16	27
1	3	9	16
2	3	17	17
0	4	19	15
2	4	17	16
0	5	14	6
2	5	17	16
0	6	18	15
1	6	12	11
2	6	14	17
0	7	24	18
2	7	12	15
0	8	13	12
1	8	6	6
l=16			
0	0	21	22
1	0	32	34
2	0	10	10
1	2	19	15
1	4	16	16
0	6	11	7
1	6	19	21
l=17			
0	1	14	16
l=18			
0	0	33	38
1	0	9	11
2	0	12	13
0	2	26	22
2	2	12	11
0	3	19	19
2	3	7	12
0	4	18	12
0	5	12	13
l=19			
1	0	21	23
1	1	12	17
1	2	19	23

Table III

Molecular Parameters

Atoms	Molecule A	Molecule B	Molecule C
	Distance, Å		
Fe–C(1)	1.82 (4)	1.84 (4)	1.80 (4)
Fe–C(2)	2.09 (3)	2.06 (3)	2.03 (3)
Fe–C(4)	1.84 (4)	1.85 (3)	1.81 (4)
C(1)–O(1)	1.14 (4)	1.09 (5)	1.11 (5)
C(4)–O(4)	1.11 (5)	1.11 (4)	1.14 (5)
C(2)–C(2)′	1.40 (5)	1.30 (4)	1.40(4)
C(2)–C(3)	1.49 (5)	1.52 (5)	1.53 (5)
C(3)–O(2)	1.21 (4)	1.28 (5)	1.22 (5)
C(3)–O(3)	1.30 (4)	1.27 (4)	1.29 (4)
	Angle, Deg		
O(1)–C(1)–Fe	176.2 (3.2)	172.1 (3.4)	173.7 (3.5)
O(4)–C(4)–Fe	171.2 (3.2)	173.7 (3.0)	174.3 (3.5)
C(1)–Fe–C(1)′	176.7 (1.7)	178.1 (1.6)	171.3 (1.8)
C(4)–Fe–C(4)′	107.5 (1.8)	116.6 (1.7)	109.2 (1.8)
C(1)–Fe C(4)	88.7 (1.6)	90.0 (1.5)	85.5 (1.8)
C(1)–Fe–C(2)	96.8 (1.7)	96.3 (1.5)	94.7 (1.5)
C(1)–Fe–C(2)′	86.4 (1.7)	85.5 (1.5)	93.4 (1.5)
C(4)–Fe–C(2)	107.4 (1.5)	104.1 (1.3)	105.3 (1.5)
C(2)–Fe–C(2)′	39.0 (1.4)	36.5 (1.2)	40.3 (1.2)
Fe–C(2)–C(3)	109.3 (3.1)	110.6 (3.0)	115.9 (3.3)
C(2)′–C(2)–C(3)	114.8 (3.5)	121.2 (3.5)	121.4 (2.7)
C(2)–C(3)–O(2)	126.8 (3.1)	117.1 (2.9)	115.6 (3.0)
C(2)–C(3)–O(3)	111.3 (2.8)	118.5 (2.8)	112.3 (3.0)
O(2)–C(3)–O(3)	121.8 (2.9)	124.3 (2.9)	131.9 (3.4)
C(3)–C(2)–C(2)′, C(2)–C(2)′–C(3)	154.2 (2.6)	153.1 (2.7)	142.5 (2.9)

Table IV

Bijvoet Pairs Utilized for the Determination of the Absolute Configuration $I(\mathrm{A}) > I(\mathrm{B})$

A	B	A	B	A	B	A	B
121	$12\bar{1}$	$1\bar{3}3$	$1\bar{3}\bar{3}$	$27\bar{3}$	273	$1\bar{4}5$	145
141	$14\bar{1}$	$1\bar{3}4$	$1\bar{3}\bar{4}$	$2\bar{3}3$	$2\bar{3}\bar{3}$	$1\bar{7}5$	175
$15\bar{1}$	151	243	$24\bar{3}$	144	$1\bar{4}4$	$1\bar{5}7$	157
$16\bar{1}$	161	253	$25\bar{3}$	115	$1\bar{1}5$	158	$1\bar{5}8$
$14\bar{2}$	142	263	$26\bar{3}$	$1\bar{2}5$	125	$1\bar{2}4$	124

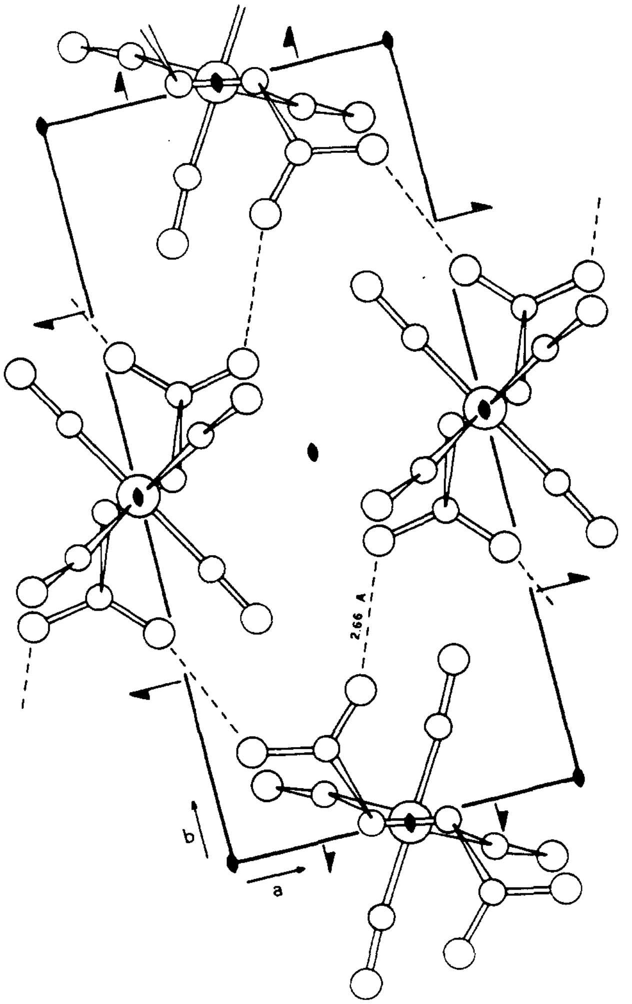

Figure 2.—Packing model of "A" type molecules viewed along the *c* axis.

using anisotropic thermal parameters for the iron atoms only. The following weighting scheme was used: $w = 1/(A + BF_o + CF_o^2)$ $(A = 0.11111;\ B = 1/(18.0F_o(\mathrm{min}));\ C = 2/(18.0F_o(\mathrm{min})F_o(\mathrm{max}))$, where F_o(min) and F_o(max) are, respectively, the minimum the maximum values of the observed structure factors. The final R factor is 11.6%. The data were also refined using anisotropic thermal parameters for all the atoms. The final R was 9.2%.

There are no relevant differences between the two final sets of coordinates. However, not much significance may be attached to the anisotropic thermal parameters of carbon and oxygen atoms. We report, therefore, the data relative to the partially anisotropic treatment. A final difference synthesis calculated with these data shows a few scattered peaks of a maximum 0.9 e$^-$/Å^3 electron density.

Determination of the Absolute Configuration

The anomalous diffraction of the iron atom with Cu Kα radiation was utilized to determine the absolute configuration of the molecule. The 1*kl* and 2*kl* reflections, photographically recorded by the integrating equiinclination Weissenberg method, were analyzed. Significant differences in the intensities of 20 Bijvoet pairs were found. The comparison was made visually

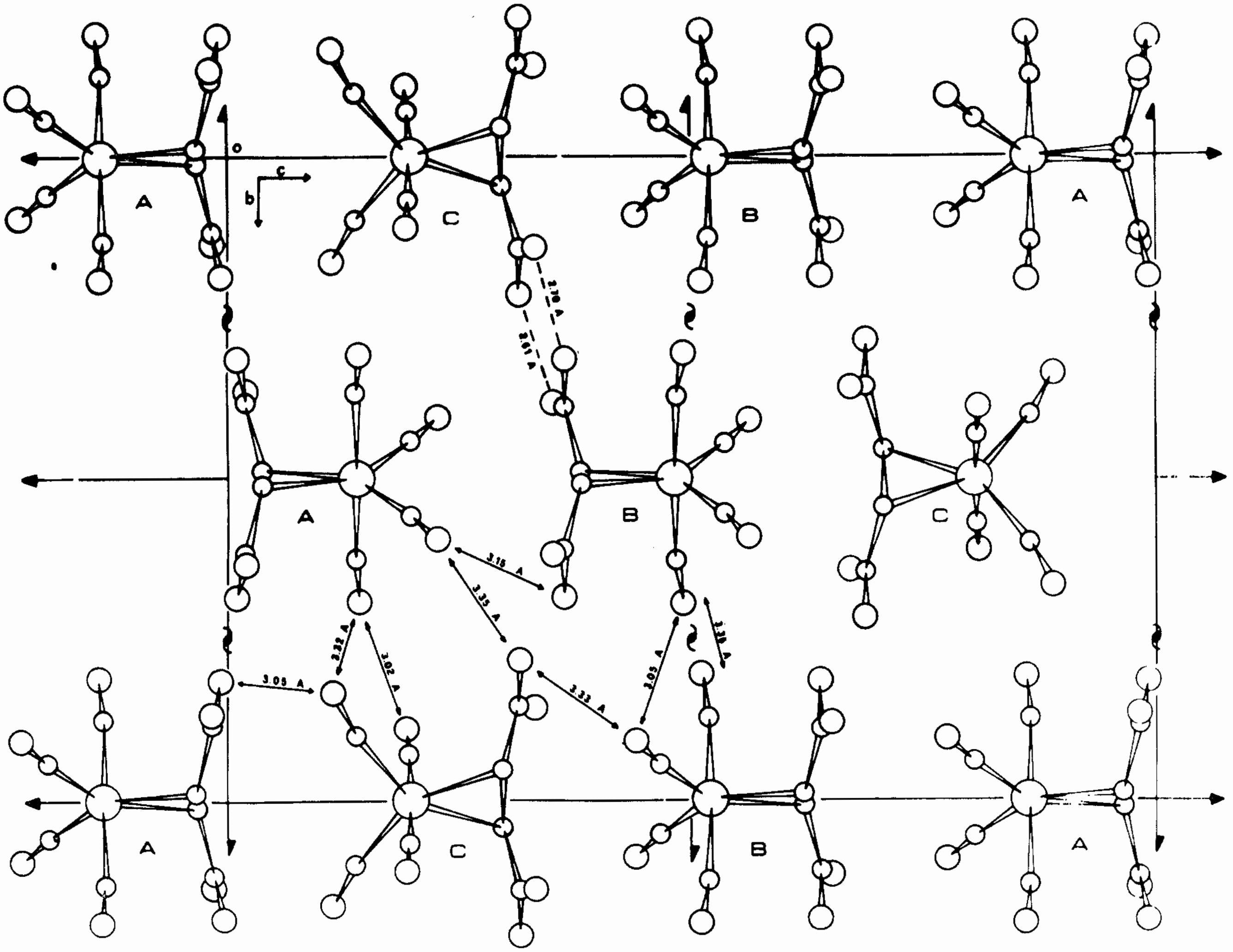

Figure 3.—Complete packing model of the molecules of (−)-$Fe(CO)_4(CHCOOH)_2$ viewed along the *a* axis.

and independently by both authors. A third analysis was performed with a photometer connected to a graphic recorder. The results obtained are in accordance with the values calculated with the coordinates of Table I. The value of the imaginary contribution of the iron atom scattering factor used in the calculation is $\Delta F = 3.4$.[13] The coordinates of Table I correspond to the configuration found. According to the sequence rule used by Cahn, Ingold, and Prelog[14] the absolute configuration of the asymmetric centers of (−)-$Fe(CO)_4(CHCOOH)_2$ may be described as *R*,*R*.

Description and Discussion of the Structure

Both the molecular and the crystal structure of (−)-$Fe(CO)_4(CHCOOH)_2$ (see Figure 1) exhibit some interesting features. The configuration of the ligands around the iron atom is nearly trigonal bipyramidal as in the racemic form. However, the conformations of the three independent molecules (called A, B, C) in the optically active crystals are slightly but significantly different from one another. A common structural characteristic of the molecules both in the racemic and optically active forms is the noncoplanarity of the carbon atoms of the fumaric acid group. The internal rotation angles around the –CH=CH– bond are 154.2, 153.1, and 142.5°, respectively for the molecules of A, B, and C types. The reason for the distortion seems to be the necessity of a relaxation of the intramolecular contact distance between the carbon atom of the carboxylic group and that of the apical carbonyl. This distance which is actually 3.0 Å would be about 2.7 Å if the fumaric acid group were planar. The least-squares plane for (equally weighted) atoms C(2)C(2)′–C(4)C(4)′–O(4)O(4)′ of each independent molecule has been calculated. The equations are: $-0.0863X + 0.1496Y = 1$ (for molecule A), $-0.1028X + 0.1965Y = 1$ (for molecule B), and $-1.833X + 0.9857Y = 1$ (for molecule C). No significant deviation from the plane is observed in molecules of the C type (maximum deviation 0.05 Å for C(2C)). This conformation closely corresponds to that found by Luxmoore and Truter[15] for tetracarbonylacrylonitrileiron and the qualitative explanation given by those authors can be directly transferred to our case. Significant deviations from the least-squares plane are observed for the carbon atoms of the –CH=CH– group of the A and B molecules. The deviation of 0.20 Å for C(2A) and C(2B) cor-

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(13) C. H. Dauben and D. H. Templeton, *Acta. Cryst.*, **8**, 841 (1955).

(14) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

(15) A. R. Luxmoore and M. R. Truter, *Acta Cryst.*, **15**, 1117 (1962).

responds to a rotation of the –CH=CH– group around the coordination axis of 17° for both molecules.

Relatively low energies should be involved in such rotations since the formation of hydrogen bonds seems to be responsible for the stable occurrence of different conformational isomers. The crystal structure appears also largely determined by the hydrogen bonding between carboxylic groups. Two different patterns of hydrogen bonding are observed. For the sake of simplicity one of them is shown in a separate figure (Figure 2). Each "A" molecule is bonded to four others of the same type. Carbon atoms and oxygen atoms of neighboring CHCOOH groups correlated by the screw axis lie on a plane. All deviations from the least-squares plane ($0.0997Y + 0.5109Z = 1$) are less than 0.03 Å. A complete packing model projected along the a axis is shown in Figure 3. Crystallographically independent molecules of the B and C types are hydrogen bonded. The carbon and oxygen atoms of two CHCOOH groups connected by hydrogen bonds are also practically planar.

Acknowledgment.—The Preliminary calculations were carried out with programs furnished by Giglio and Damiani.[16] For the final refinement of the structure the programs were kindly supplied by Vaciago and Domenicano[17] to whom A. S. is particularly grateful for many computing facilities. We are grateful, as well, to R. Palumbo, who furnished the compound, and to Professor P. Corradini, for stimulating discussion and help, especially at the first stage of the work.

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[16] A. Damiani, F. De Santis, E. Giglio, and A. Ripamonti, *Ric. Sci., Rend., Sez. A*, **33**, 965 (1963).

[17] V. Albano, A. Domenicano, and A. Vaciago, *Gazz. Chim. Ital.*, **96**, 922 (1966).

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The Crystal Structure of μ-Chloro-bis(chlorotetra(benzimidazole)nickel(II)) Chloride–4-Acetone[1]

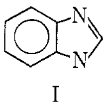
By MICHAEL G. B. DREW, DAVID H. TEMPLETON, and ALLAN ZALKIN

Received April 8, 1968

The crystal structure of μ-chloro-bis(chlorotetra(benzimidazole)nickel(II)) chloride–4-acetone has been determined by single-crystal X-ray techniques. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions $a = 12.551$ (5), $b = 16.517$ (7), $c = 17.794$ (7) Å, $\beta = 106.72$ (5)°. The unit cell contains two cations of formula $Ni_2Cl_3(C_7H_6N_2)_8^+$, two chloride ions Cl^-, and eight molecules of acetone. The observed and calculated densities are 1.35 ± 0.01 and 1.354 g cm^{-3}, respectively. The intensities of 2492 reflections above background were collected by counter methods and the structure has been refined to a conventional R factor of 0.101. The cations are of the form $Cl\text{–}Ni(C_7H_6N_2)_4\text{–}Cl\text{–}Ni(C_7H_6N_2)_4\text{–}Cl^+$, with the bridging chlorine atom on a center of symmetry. The Cl–Ni–Cl–Ni–Cl chain is closely linear (Cl–Ni–Cl = 179.3 (1)°), and the two nickel–chlorine distances are appreciably different (Ni–Cl(terminal) = 2.425 (4) Å, Ni–Cl(bridging) = 2.941 (2) Å).

Introduction

During studies[2,3] of the nickel(II) complexes with benzimidazole (I), three compounds, colored blue, green, and olive green, of the general formula $Ni(C_7H_6N_2)_4Cl_2((CH_3)_2CO)_2$ were prepared. These three compounds had differing magnetic properties, with magnetic moments of 3.15, 3.06, and 2.35 BM at room temperature and Weiss constants of −8, −77, and −400°, respectively. The green compound held to Curie–Weiss behavior over the range 200–300°K: in the range 100–200°K, deviation from the law is small but on reaching 100°K, the susceptibility values show a sudden drop and the initially crystalline solid is found to be reduced to an amorphous powder without loss of acetone. In order to form a reference point for consideration of these compounds, the crystal structure of the green complex has been determined by three-dimensional X-ray analysis.



I

Experimental Section

Crystals of the green compound, immersed in acetone, were provided by Dr. M. J. Weeks. Preliminary photographs by the Weissenberg technique showed a monoclinic lattice. The cell dimensions were measured at room temperature (~23°) with a General Electric quarter-circle goniostat (λ 0.70926 Å for Mo $K\alpha_1$). They are $a = 12.551$ (6), $b = 16.517$ (7), $c = 17.794$ (7) Å, $\beta = 106.72$ (5)°. The errors in the last digits (in parentheses) are subjective estimates of the standard deviations. The observed density (by flotation in a mixture of benzene and ethylene bromide) is 1.35 ± 0.01 g cm^{-3}. The calculated density for two formula units of $[Ni_2Cl_3(C_7H_6N_2)_8]Cl \cdot 4(CH_3)_2CO$ in the unit cell is 1.354 g cm^{-3}. The Weissenberg photographs show that reflections are absent for $h0l$ if $l = 2n + 1$ and for $0k0$ if $k = 2n + 1$. These rules are characteristic of space group $P2_1/c$ and this choice is confirmed by the structure determination.

The diffraction data were obtained from a crystal of approximate dimensions 0.4 × 0.3 × 0.3 mm mounted with b parallel

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] M. J. Weeks, Ph.D. Thesis, University of London, 1966.

[3] D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc., A*, 1125 (1967).