parameters that have not been extensively examined (electron repulsions, steric interference, etc., might be advanced).

Acknowledgment. The authors are grateful for the assistance of Dr. David Goldsmith with the mass spectra and Dr. Gogi Kodama with the ^{11}B nmr spectra. Appreciation is also expressed to the Air Force for the use of a Jeol 60-MHz nmr at Robins Air Force Base. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $PF_2CH{=}CH_2$, 51130-03-1; PF_2Br, 15597-40-7; $(CH_2{=}CH)_2Hg$, 1119-20-6; $PF_2CH{=}CH_2{\cdot}BH_3$, 51130-04-2; B_2H_6, 19287-45-7.

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Magnetic Behavior of Some Polynuclear Methoxide Complexes of Iron(III) with Meta-Substituted Benzoates

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The interest in recent years in alkoxide as a ligand has resulted in the synthesis of a number of polynuclear complexes of tervalent iron. The presence of bridging alkoxide usually leads to antiferromagnetic coupling between the metal atoms. Antiferromagnetic trimeric *n*-alkoxides $(Fe_3(OR)_9)^{1-3}$ have been characterized. Kakos and Winter[4] prepared the antiferromagnetic trimer $FeCl(OMe)_2$ and the tetramers $Fe_4X_6(OMe)_6{\cdot}4MeOH$ and $Fe_4X_3(OMe)_9$, where X is Cl or Br. In previous papers we have described compounds of the type $FeL(OMe)_2$. All the compounds are antiferromagnets. The complex with L = acetylacetonate is probably a dimer.[5] The others for which L is alkanoate[6] and aromatic acid[7] are probably tetramers. All compounds show a single C-O stretching band. A structure involving trigonal prismatic iron atoms was found to agree best with the experimental evidence. We now report the results on complexes of the same type where L is meta-substituted benzoate.

Experimental Section

All complexes were prepared according to Kokot, *et al.*[5] They are all yellow, unstable to heat above 250°, insoluble in organic solvents and moisture sensitive. Iron was determined volumetrically with potassium dichromate and sodium diphenylaminesulfonate indicator. Carbon and hydrogen were determined in The University of New South Wales Microanalytical Laboratory and by the Australian Microanalytical Service (Melbourne).

Physical Measurements. Magnetic measurements were carried out as described previously.[8] The infrared spectra in KBr were recorded with a Jasco DS 4039 infrared spectrophotometer between 4000 and 300 cm^{-1}. The electronic reflectance spectra were obtained with a Zeiss PMQ II spectrophotometer fitted with an RA-3 reflectance

Table I. Magnetic Data at Various Temperatures of Complexes

Temp, °K	$10^6\chi_A$, cgsu	μ, BM	Temp, °K	$10^6\chi_A$, cgsu	μ, BM
m-Methylbenzoate ($-10^6\Delta = 117$)					
78.5	17,036	3.28	220.0	11,716	4.56
95.5	16,387	3.55	250.0	10,828	4.67
110.0	15,759	3.74	280.0	10,088	4.77
130.0	14,936	3.96	295.8	9,715	4.79
150.0	14,165	4.14	310.0	9,421	4.85
170.0	13,427	4.29	340.0	8,817	4.92
195.0	12,517	4.44			
m-Methoxybenzoate ($-10^6\Delta = 121$)					
78.5	18,614	3.43	220.5	12,266	4.67
95.0	17,765	3.69	250.0	11,263	4.76
109.5	17,124	3.89	280.5	10,466	4.86
132.5	16,060	4.14	295.5	10,106	4.89
150.0	15,155	4.28	310.0	9,764	4.94
170.0	14,277	4.42	340.5	9,096	5.00
195.5	13,195	4.56			
m-Chlorobenzoate ($-10^6\Delta = 119$)					
78.0	18,274	3.39	220.5	12,364	4.69
95.5	17,599	3.68	250.0	11,386	4.79
110.0	16,985	3.88	280.0	10,605	4.89
130.5	16,076	4.11	296.9	10,185	4.92
150.0	15,191	4.29	310.0	9,845	4.96
170.0	14,321	4.43	340.0	9,242	5.03
195.5	13,264	4.57			
m-Nitrobenzoate ($-10^6\Delta = 112$)					
81.5	14,440	3.08	220.5	10,962	4.41
97.0	14,246	3.34	250.0	10,247	4.54
110.5	13,924	3.52	280.0	9,556	4.64
131.0	13,571	3.79	295.5	9,237	4.67
150.5	13,016	3.97	310.0	8,979	4.74
170.5	12,436	4.13	340.0	8,443	4.81
195.5	11,705	4.29			

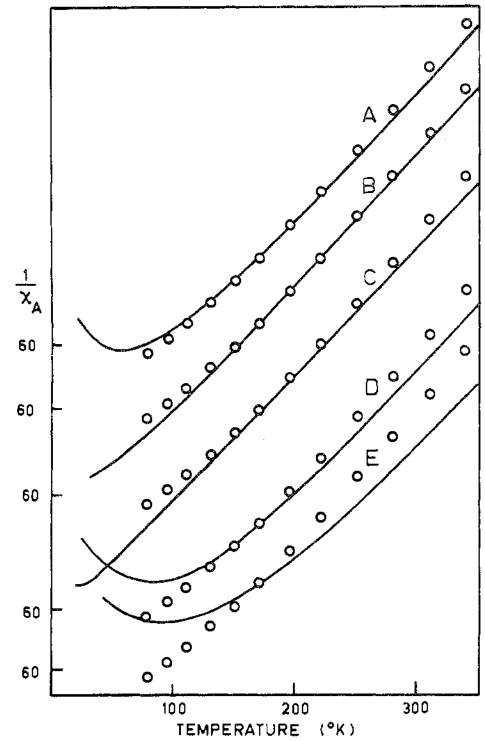

Figure 1. Comparison of best-fit $\chi_A^{-1}(T)$ curves for the *m*-methylbenzoate complex for the following cluster models: Fe_4 planar (A), Fe_4 tetrahedral (B), Fe_3 equilateral triangle (C), infinite chain (D), and Fe_2 (E).

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Table II. Carboxylate (OCO) and Methoxide (CO) C–O Stretching Frequencies of the Complexes (cm^{-1}) and Analytical Data

				Analyses,[a] %					
				C		H		Fe	
Ligand	ν_{as}(OCO)	ν_s(OCO)	ν(CO)	Found	Calcd	Found	Calcd	Found	Calcd
m-Methylbenzoate	1525	1400	1045	47.4	47.1	5.1	5.0	22.1	22.0
m-Methoxybenzoate	1530	1405	1038	44.6	44.3	4.8	4.8	20.8	20.6
m-Chlorobenzoate	1530	1400	1038	39.5	39.4	3.7	3.9	20.5	20.4
m-Nitrobenzoate[a]	1535	1408	1043	38.0	37.7	3.5	3.5	19.7	20.1

[a] Nitrogen analysis: calcd, 4.9%; found, 5.0%.

attachment in the range 6000–25,000 cm^{-1}. The experimental data are tabulated in Tables I and II.

Results and Discussion

Magnetism. The complexes are antiferromagnets. Their magnetic behavior is very similar to that of the alkanoate[6] and aromatic acid[7] analogs described earlier. The magnetic moments at room temperature fall in the range 4.67–4.92 BM (Table I) well below 5.9 BM expected for high-spin iron(III) and with falling temperature the reciprocal susceptibility curves up toward higher values. Calculated susceptibilities were fitted to experimental values using equations based on the following cluster models: dimer,[9] equilateral[10] and isosceles[4] triangle trimers, tetrahedral[4] and planar[4] tetramers, and linear chain.[11] Values of $g = 2.0$ and $N\alpha = 0$ were used as required by the $^6A_1$ ground state of high-spin iron(III). Best-fit J values are listed in Table III. Best-fit theoretical $\chi^{-1}(T)$ curves for the various cluster models are compared for *m*-methylbenzoate in Figure 1. The planar tetramer equation gives the best fit in all cases with $J_A = J_B = J_C$ for the three J values required by this cluster model. A good fit is also given by the tetrahedral tetramer model. A structure involving a tetrahedral disposition of iron atoms is however not supported by the infrared evidence which points to the presence of only one type of methoxy group. The isosceles triangle model was inapplicable in all cases. For all complexes the slope of the experimental $\chi^{-1}(T)$ curves is slightly steeper than of the theoretical curves, possibly due to hydrolysis products. Adams, *et al.*,[2] found that for the iron(III) alkoxides the slope increased with progressive hydrolysis.

Table III. Best-Fit J Values (cm^{-1}) for the Complexes for Various Cluster Models

Ligand	Fe_4 planar $-J_A = -J_B = -J_C$	Fe_4 tetr $-J$	Fe_3 equil triangle $-J$	Inf chain $-J$	Fe_2 $-J$
m-Methylbenzoate	3.8	5.3	7.4	6.8	11.0
m-Methoxybenzoate	3.5	4.7	6.7	6.5	10.5
m-Chlorobenzoate	3.4	4.7	6.5	6.3	10.5
m-Nitrobenzoate	4.4	6.0	8.5	7.8	13.0

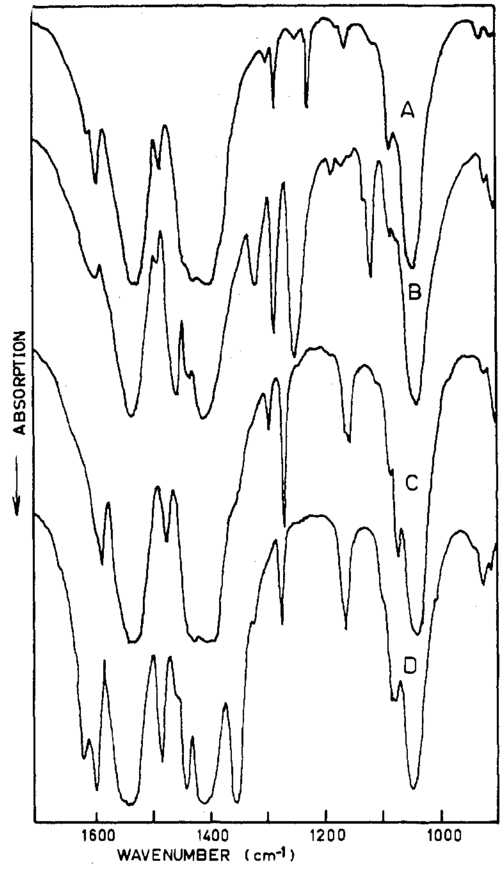

Figure 2. Infrared spectra (1700–900 cm^{-1}): *m*-methylbenzoate (A), *m*-methoxybenzoate (B), *m*-chlorobenzoate (C), *m*-nitrobenzoate (D).

Infrared Spectra. The bands which are of most interest are the C–O stretching of the carboxylate and methoxide groups (Table II, Figure 2). The carboxyl group may act as a uni- or bidentate ligand. When it acts as a bidentate ligand, it may chelate or form a bridge between two metal atoms.[12–14] According to the arguments of Curtis[15] the well-defined asymmetric band at 1540 cm^{-1} and the symmetric band at 1435 cm^{-1} suggest a bidentate carboxyl group. Similar values for the two bands were recorded for other alkanoate[6] and aromatic acid[7] complexes of the same type. In dimeric β-diketone complexes of the type $[FeL_2(OMe)]_2$ the single C–O stretching band at ~1050 cm^{-1} [16] was assigned to methoxide bridging two six-coordinate iron atoms. A single C–O stretching band in the region 1038–1052 cm^{-1} is present in complexes of the type $FeL(OMe)_2$ described earlier.[5–7] The present complexes show similarly only one C–O stretching band at 1040–1048 cm^{-1} in the region in which methoxide bridging two six-coordinate iron(III) atoms absorbs.[16]

Electronic Reflectance Spectra. The complexes show bands in the regions 10,000, 15,000, 19,000, and 22,000 cm^{-1} similar to the alkanoate[6] and aromatic acid[7] analogs in agreement with the presence of six-coordinate iron(III).

Proposed Structure. A structure which agrees with the general applicability of the planar tetrameric cluster model to the magnetic behavior and which also meets the requirement of equivalent methoxide groups, bidentate carboxylate, and six-

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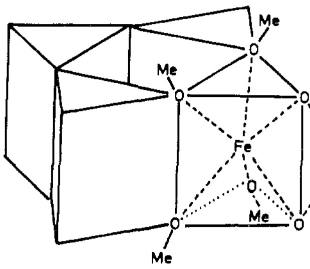
coordinate iron(III) is a cluster of four trigonal-prismatic iron atoms sharing parallel edges (I).



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Registry No. Fe(*m*-methylbenzoate)(OMe)$_2$, 50803-72-0; Fe(*m*-methoxybenzoate)(OMe)$_2$, 50803-73-1; Fe(*m*-chlorobenzoate)(OMe)$_2$, 50803-70-8; Fe(*m*-nitrobenzoate)(OMe)$_2$, 50803-71-9.

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Bis(trifluoromethyl)phosphino Derivatives of *closo*-2,4-Dicarbaheptaborane(7)

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The derivative chemistry of the lighter carboranes is worthy of considerable further development; for instance, their phosphino derivatives should be interesting either as ligands for transition element complexes or for making new inorganic polymer systems. A major difficulty is the relatively high reactivity of the lighter carboranes, such that they may easily convert to intractable resins under conditions (*e.g.*, presence of a base) tolerated by the larger carboranes. For example, the carbon base $LiC(CH)B_5H_5$ is seriously unstable in solution, and $(LiC)_2B_5H_5$ may be largely destroyed in attempts to make derivatives from it,[1] whereas alkali "salts" of $C_2B_{10}H_{12}$ can be used for high-yield syntheses of many derivatives.[2]

The present study led to the synthesis of three derivatives in which the $(CF_3)_2P$ group is attached to carbon in the $C_2B_5H_7$ cage. Their stability may well be due in part to the lack of effective base action by the $(CF_3)_2P$ group. However, extensive destruction of the Li-C bases during the syntheses led to poor yields of $(CF_3)_2PC(CH)B_5H_5$ or $[(CF_3)_2PC]_2B_5H_5$. The difficulties may have been like those encountered when HCl attacked $(LiC)_2B_5H_5$ to give only 11% recovery of $C_2B_5H_7$, in contrast to better than 70% yields of $(CH_3C)_2B_5H_5$ by action of methyl iodide.[1] The base $LiC(CH_3C)B_5H_5$ was relatively satisfactory, reacting with $(CF_3)_2PCl$ to give a 29% yield of $(CF_3)_2PC(CH_3C)B_5H_5$. In this case, the methyl group was expected to minimize polymerization; and since the initially insoluble $LiC(CH_3C)B_5H_5$ was wholly dissolved during the reaction, occlusion did no harm.

Syntheses and Characterizations

Methods. All volatile substances were managed by means of Stock-type high-vacuum techniques. The carborane $C_2B_5H_7$ was isolated from a mixture of light carboranes kindly given to us by Drs. R. E. Williams and J. F. Ditter, of Chemical Systems, Inc. The method of isolation included removal of B_5H_9 by the action of alcohols or tertiary amines. The final purification of each reaction product was by high-vacuum fractional condensation.

The Monophosphino Derivative. A commercial hexane solution of 2.0 mmol of butyllithium was mixed stepwise into a 1:1 ether-hexane solution of 1.0 mmol of $C_2B_5H_7$, at −23°. The mixture was held at −23° for 3 hr and then stirred for 15 hr at 25°. The solvent was removed from the precipitated $(LiC)_2B_5H_5$ and replaced by 2 ml of fresh ether, followed by 1.0 mmol of $(CF_3)_2PI$. The mixture was stirred first at −95° and then at 25° for 1 hr. Now the second Li-C bond was converted to H-C by action of 1.1 mmol of HCl, added at −196° and allowed to react during slow warming to 25°, with stirring. It now was possible to isolate 0.20 mmol of an equimolar mixture of $C_2H_5OP(CF_3)_2$ and $(CF_3)_2PC(CH)B_5H_5$. The ethoxyphosphine (formed by unavoidable cleavage of the ether and hard to remove by distillation) was absorbed by Al_2Cl_6 (10 min, 25°), with some destruction of the desired product: final yield, 0.05 mmol, or 5%. When $(CF_3)_2PCl$ was used for the action upon $(LiC)_2B_5H_5$ (in 1:1 molar ratio), the ether cleavage did not occur, but both the mono- and diphosphino derivatives were formed, in far inferior yields.

The new compound $(CF_3)_2PC(CH)B_5H_5$ showed an equilibrium vapor pressure of 10 mm at 25°. Its formula was confirmed by a mass spectrographic parent peak pattern having the right mix of boron isotopic effects. Its infrared and nmr spectra proved to be consistent with the assumed structure.

The Bis(phosphino)carborane. The dilithium compound from 1.0 mmol of $C_2B_5H_7$ was treated with 2.0 mmol of $(CF_3)_2PCl$ in diethyl ether, during slow warming from −23 to +25°, with good stirring. The yield of $[(CF_3)_2PC]_2B_5H_5$ (authenticated by its mass, nmr, and infrared spectra) was 0.11 mmol, or 11%. Its volatility as a pure liquid was 0.5 mm at 0° or 2.0 mm at 25°. A trace of $(CF_3)_2PC(CH)B_5H_5$ was found as a by-product.

We next tried a procedure based upon a very successful method for making $[(CH_3)_2SiClC]_2B_5H_5$:[3] stepwise addition of 2.1 mmol of $(LiC)_2B_5H_5$ (slurry in 3 ml of ether-hexane) to 4.6 mmol of $(CF_3)_2PI$ in 1 ml of hexane (2 hr, −23°, stirred; 0.5 hr, 25°, stirred); yield of $[(CF_3)_2PC]_2B_5H_5$, 88.5 mg, or 10%.

The *C*-Methylphosphinocarborane. A 1.07 mmol sample of $CH_3C(CH)B_5H_5$, prepared according to the literature,[1] was treated with 1.32 mmol of LiC_2H_5, in 2 ml of hexane with 1 ml of ether. The mixture was stirred for 15 hr at 25°. After vacuum removal of the solvent, the white residue was suspended in 2 ml of fresh ether at −95°. Treatment with 1.2 mmol of $(CF_3)_2PCl$, during gradual warming (with periods of constancy at −78 and −23°), led to formation of 0.31 mmol (29% yield) of $(CF_3)_2PC(CH_3C)B_5H_5$, which was easily isolated and confirmed by mass, nmr, and infrared spectra. Vapor pressures: 1.0 mm at −10°, 2.0 mm at 0°, and 7.0 mm at 25°.

Acetonitrile as Solvent. The "salt" $(LiC)_2B_5H_5$, precipitated from the ether-hexane mixture, dissolved completely in CH_3CN, and HCl acted upon the fresh solution to restore

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