

- Cooper, and E. Margolash, *J. Biol. Chem.*, **246**, 1511 (1971); R. E. Dickerson, *Ann. N.Y. Acad. Sci.*, **227**, 599 (1974) (horse heart, bonito cyt. c).
- (80) F. R. Salemme, S. T. Freer, Ng. H. Xuong, R. A. Alden, and J. Kraut, *J. Biol. Chem.*, **248**, 3910 (1973) (*R. rubrum* cyt. c<sub>2</sub>).
- (81) F. S. Mathews, M. Levine, and P. Argos, *J. Mol. Biol.*, **64**, 449 (1972) (calf liver cyt. b<sub>5</sub>).
- (82) T. Shimizu, T. Nozawa, M. Hatano, Y. Imai, and R. Sato, *Biochemistry*, **14**, 4172 (1975).
- (83) Y. Miyake, K. Mori, and T. Yamano, *Arch. Biochem. Biophys.*, **133**, 318 (1969).
- (84) J. A. Whysner, J. Ramseyer, and B. W. Harding, *J. Biol. Chem.*, **245**, 5441 (1970); S. C. Cheng and B. W. Harding, *ibid.*, **248**, 7263 (1973).
- (85) (a) Reference 58, pp 215-229; (b) W. E. Blumberg and J. Pelsach, *Adv. Chem. Ser.*, No. **100**, 271 (1971).
- (86) H. A. O. Hill, A. Roder, and R. J. P. Williams, *Naturwissenschaften*, **57**, 69 (1970).
- (87) J. Pelsach, W. E. Blumberg, and A. Adler, *Ann. N.Y. Acad. Sci.*, **206**, 310 (1973).
- (88) J. Pelsach and W. B. Mims, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2979 (1973).
- (89) W. E. Blumberg, J. Pelsach, B. Hoffman, E. Stellwagen, E. Margolash, L. Marchant, J. Tulloss, and B. Feinberg, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **32**, 469 (1973); D. O. Lambeth, K. L. Campbell, R. Zand, and G. Palmer, *J. Biol. Chem.*, **248**, 8130 (1973).
- (90) It should be emphasized that detailed structural comparison between active sites or prosthetic groups in metalloproteins and synthetic analogues proposed as their minimal models is in a very formative stage. Owing to the lack of protein structural data which compare in precision to those of usual heavy-atom complex structures, such comparisons are presently limited to 1-Fe<sup>91</sup> and 4-Fe<sup>91,92</sup> iron-sulfur proteins and their synthetic analogues.<sup>93,45c,46</sup> Biological and synthetic 4-Fe clusters have nearly congruent structures whereas the 1-Fe analogue<sup>45c</sup> is an unconstrained (symmetrized) version of the Fe-S<sub>4</sub> center in rubredoxin proteins. Comparisons between forms of Mb and Hb and synthetic porphyrins have been assembled<sup>46b,93</sup> and the available protein data, while not highly precise, suggest some structural differences.
- (91) L. H. Jensen, *Annu. Rev. Biochem.*, **43**, 461 (1974).
- (92) S. T. Freer, R. A. Alden, C. W. Carter, Jr., and J. Kraut, *J. Biol. Chem.*, **250**, 46 (1975).
- (93) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4452 (1974).
- (94) B. L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. U.S.A.*, **59**, 498 (1968); R. J. P. Williams, *Inorg. Chim. Acta, Rev.*, **5**, 137 (1971).
- (95) J. A. Peterson and B. W. Griffin, *Drug Metab. Dispos.*, **1**, 14 (1973); B. W. Griffin and J. A. Peterson, *J. Biol. Chem.*, **250**, 6445 (1975).
- (96) B. W. Griffin, S. M. Smith, and J. A. Peterson, *Arch. Biochem. Biophys.*, **160**, 323 (1974).
- (97) G. C. Brackett, P. L. Richards, and W. S. Caughey, *J. Chem. Phys.*, **54**, 4383 (1971).
- (98) (a) P. F. Hollenberg and L. P. Hager, *J. Biol. Chem.*, **248**, 2630 (1973); (b) P. M. Champion, E. Münck, P. G. Debrunner, P. F. Hollenberg, and L. P. Hager, *Biochemistry*, **12**, 426 (1973); (c) R. Chiang, R. Makino, W. E. Spomer, and L. P. Hager, *ibid.*, **14**, 4166 (1975).
- (99) J. O. Stern and J. Pelsach, *J. Biol. Chem.*, **249**, 7495 (1974).
- (100) (a) J. P. Collman and T. N. Sorrell, *J. Am. Chem. Soc.*, **97**, 4133 (1975); (b) J. P. Collman, T. N. Sorrell, J. H. Dawson, J. R. Trudell, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U.S.A.*, in press.
- (101) C. K. Chang and D. Dolphin, *J. Am. Chem. Soc.*, **97**, 5948 (1975).
- (102) P. M. Champion, R. Chiang, E. Munck, P. Debrunner, and L. P. Hager, *Biochemistry*, **14**, 4159 (1975).
- (103) NOTE ADDED IN PROOF: The MCD spectrum of high-spin chloroperoxidase is highly suggestive of axial cysteinate coordination, contrary to chemical results:<sup>96c</sup> J. H. Dawson, J. R. Trudell, G. Barth, R. E. Linder, E. Bunnenberg, C. Djerassi, R. Chiang, and L. P. Hager, *J. Am. Chem. Soc.*, submitted for publication.

## The Crystal Structure of Na<sub>2</sub>Fe(CO)<sub>4</sub>·1.5(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>). Distortion of the [Fe(CO)<sub>4</sub>]<sup>2-</sup> Anion in the Solid State

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**Abstract:** The structure of Na<sub>2</sub>Fe(CO)<sub>4</sub>·1.5(dioxane) has been solved by single-crystal x-ray diffraction methods. The most notable feature of the structure is the fact that the [Fe(CO)<sub>4</sub>]<sup>2-</sup> anion is significantly distorted from tetrahedral symmetry: one of the C-Fe-C angles is 129.7°. There are basically two types of interactions between Na<sup>+</sup> and [Fe(CO)<sub>4</sub>]<sup>2-</sup> ions: short-range Na-O interactions occurring at a distance of 2.32 Å and long-range Na...C and Na...Fe interactions occurring at distances of 2.95 and 3.09 Å, respectively. Two Na<sup>+</sup> ions and two [Fe(CO)<sub>4</sub>]<sup>2-</sup> ions come together to form a curious, loosely held "cluster" in which each Na<sup>+</sup> ion is associated with the C-Fe-C regions of the anions. This unanticipated interaction between Na<sup>+</sup> and the C-Fe-C portion of [Fe(CO)<sub>4</sub>]<sup>2-</sup> is probably responsible for the distortion of the C-Fe-C angle. The geometry of the Na<sup>+</sup>...C-Fe-C region in this compound reflects the structural changes that take place in the [Fe(CO)<sub>4</sub>]<sup>2-</sup> anion when a sodium ion is brought into close proximity, and suggests that some type of angular distortion may be occurring when [Fe(CO)<sub>4</sub>]<sup>2-</sup> ion-pairs with Na<sup>+</sup> in solution. Crystallographic details for Na<sub>2</sub>Fe(CO)<sub>4</sub>·1.5(dioxane) are: space group *P4<sub>2</sub>/m* (tetragonal), *a* = 10.690 (5) Å, *c* = 12.283 (6) Å, and *Z* = 4. Final *R* factor is 6.1% for 1175 independent reflections.

The application of Na<sub>2</sub>Fe(CO)<sub>4</sub> as a "transition metal analogue of the Grignard reagent" has been vigorously explored by Collman and his co-workers during the past few years.<sup>2-4</sup> Many of the early synthetic applications of the potassium salt of the [Fe(CO)<sub>4</sub>]<sup>2-</sup> ion were reported by Takegami, Watanabe, and co-workers during the late 1960's,<sup>5</sup> but initial investigations of these reactions were often complicated by the questionable purity of the carbonyl compound. The recent development of a convenient synthesis of high-quality Na<sub>2</sub>Fe(CO)<sub>4</sub><sup>6</sup> has made possible a more systematic investigation of the synthetic utility of the carbonyl compound and a study of the mechanism of the reaction of the compound with organic substrates.<sup>2,7</sup>

In the course of mechanistic studies on [Fe(CO)<sub>4</sub>]<sup>2-</sup> salts and their derivatives, it was noticed that the rates of many reactions involving these compounds were markedly depen-

dent on the coordinating ability of the solvent and often also on the nature of the counterion. These observations were interpreted to indicate that tight ion pairs were being formed in solution between the alkali metal cations and the iron carbonylate anions.<sup>3</sup>

Ion pairing between metal carbonylate anions and alkali metal cations has long been suspected to exist in certain solutions,<sup>8</sup> although early investigations of the infrared spectra of [Co(CO)<sub>4</sub>]<sup>-</sup> and [Fe(CO)<sub>4</sub>]<sup>2-</sup> in water indicated the exclusive presence of tetrahedral ions,<sup>9</sup> it soon became evident that the carbonyl stretching region of these anions is highly solvent dependent. Thus NaCo(CO)<sub>4</sub> in THF (tetrahydrofuran) shows three bands in the ν<sub>CO</sub> region, while in water and DMF (*N,N*-dimethylformamide) solutions only a single band is observed.<sup>8</sup> This in addition to conductivity data<sup>10</sup> suggested that ion pairs were being formed to vary-

**Table I.** Crystal Data for  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5\text{C}_4\text{H}_8\text{O}_2$ 

Space group = $P4_2/m$ (No. 84)
$a = b = 10.690$ (5) Å
$c = 12.283$ (6) Å
$V = 1403.7$ Å <sup>3</sup>
$Z = 4$
$\rho_{\text{calcd}}^a = 1.631$ g/cm <sup>3</sup>
$\mu = 11.2$ cm <sup>-1</sup> (for Mo $K\alpha$ x rays)

<sup>a</sup> An observed density could not be measured because of the high reactivity of the compound.

ing degrees in some of the solvent systems studied. In the solid state, the geometry of  $[\text{Co}(\text{CO})_4]^-$  was found to depend somewhat on the nature of the counterion: with large cations such as  $[(\text{Ph}_3\text{P})_2\text{N}]^+$  and  $[\text{Mg}(\text{THF})_6]^{2+}$ ,  $[\text{Co}(\text{CO})_4]^-$  shows essentially a tetrahedral structure,<sup>11,12</sup> while with  $\text{Ti}^+$  significant distortion of the Co-C-O angle occurs.<sup>13</sup>

In  $\text{Na}_2\text{Fe}(\text{CO})_4$ , ion association is expected to be much more pronounced due to the greater basicity and charge density of the dianion. Studies have suggested that the predominant species in THF is the undissociated salt, while in solvents of greater coordinating ability, such as DMF, the singly dissociated species,  $[\text{NaFe}(\text{CO})_4]^-$ , is suspected to be present.<sup>7</sup> The purpose of this investigation was to determine if evidence of ion pairing could be found in the solid-state structure of  $\text{Na}_2\text{Fe}(\text{CO})_4$ .

### Crystallographic Section

Crystals of  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5(\text{C}_4\text{H}_8\text{O}_2)$  are very pale yellow

low bipyramids with a near-octahedral morphology.<sup>14</sup> A specimen with dimensions  $0.47 \times 0.47 \times 0.44$  mm was mounted in a glass capillary under an inert atmosphere. Precession photographs indicated a tetragonal crystal system with systematic absences consistent with space group  $P4_2/m$  (No. 84). The unit cell parameters, which are given in Table I together with other crystallographic details, were obtained by carefully measuring the setting angles of 24 reflections on a Nonius CAD-3 automated diffractometer.

Two octants of data were collected by the  $\theta/2\theta$  scan technique with Zr-filtered Mo  $K\alpha$  radiation up to a  $2\theta$  limit of  $50^\circ$ . A scan speed of  $10^\circ/\text{min}$  was used, with the scan defined as  $\Delta\theta = (1.2 + 0.15 \tan \theta)^\circ$ . Each reflection was scanned between two and ten times, depending on its intensity. Background counts were taken at the beginning and the end of each scan. The takeoff angle used was  $4^\circ$ , and zirconium foil attenuators were automatically inserted to prevent the counting rate from exceeding 2500 counts/s. As a check on the stability of the diffractometer and the crystal, the (4,1,3), (2,6,0), and (5,0,3) reflections were measured at 40-reflection intervals during data collection. No significant variation in these monitor intensities was observed. An empirical absorption correction was applied to the data based on the variation in intensity of an axial reflection (at  $\chi = 90^\circ$ ) with the spindle angle  $\phi$ . The absorption coefficients obtained in this manner ranged from 0.953 to 1.044 (normalized to unity).<sup>15</sup>

A total of 2961 reflections was collected and merged; 1175 unique reflections having intensities greater than  $3\sigma$  were retained for the subsequent structure analysis. The standard deviation of each intensity reading,  $\sigma(I)$ , was estimated using the expression<sup>16a</sup>  $\sigma(I) = [(peak + background$

**Table II.** Final Atomic Parameters for  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5\text{C}_4\text{H}_8\text{O}_2$  (standard deviations in parentheses)

Atom	A. Atomic Positions (in fractional coordinates)		
	x	y	z
Fe	0 <sup>a</sup>	$\frac{1}{2}$ <sup>a</sup>	0.2098 (1)
C(1)	-0.0682 (5)	0.3696 (5)	0.1497 (4)
C(2)	0.1161 (6)	0.4415 (5)	0.2948 (4)
C(3)	0.4327 (5)	0.4792 (6)	0.0972 (5)
C(4)	0.1592 (7)	0.0628 (5)	0.0970 (5)
C(5)	0.2470 (6)	0.1714 (6)	0.0969 (5)
O(1)	-0.1176 (4)	0.2763 (4)	0.1230 (4)
O(2)	0.1944 (5)	0.4048 (4)	0.3531 (4)
O(3)	0.4732 (5)	0.3690 (5)	$\frac{1}{2}$ <sup>a</sup>
O(4)	0.0122 (5)	0.1807 (6)	$\frac{1}{2}$ <sup>a</sup>
O(5)	0.2266 (5)	0.2461 (4)	0 <sup>a</sup>
Na(1)	0.2120 (3)	0.2698 (3)	$\frac{1}{2}$ <sup>a</sup>
Na(2)	0.1478 (3)	0.4415 (3)	0 <sup>a</sup>

Atom	B. Anisotropic Temperature Factors <sup>b</sup>					
	$10^4 \beta_{11}$	$10^4 \beta_{22}$	$10^4 \beta_{33}$	$10^4 \beta_{12}$	$10^4 \beta_{13}$	$10^4 \beta_{23}$
Fe	48 (1)	42 (1)	23 (1)	-2 (2)	0 <sup>c</sup>	0 <sup>c</sup>
C(1)	72 (5)	85 (5)	35 (3)	-17 (8)	-9 (6)	-14 (7)
C(2)	107 (6)	60 (5)	58 (4)	-20 (9)	-46 (8)	11 (7)
C(3)	71 (5)	134 (7)	41 (4)	-22 (9)	-4 (7)	14 (8)
C(4)	155 (8)	78 (5)	54 (4)	-21 (10)	17 (9)	14 (8)
C(5)	135 (7)	80 (6)	61 (4)	-24 (10)	-60 (9)	29 (8)
O(1)	154 (6)	132 (5)	63 (3)	-134 (9)	-21 (7)	-48 (7)
O(2)	160 (6)	111 (5)	99 (4)	-3 (9)	-153 (9)	61 (7)
O(3)	105 (6)	60 (5)	60 (4)	8 (9)	0 <sup>c</sup>	0 <sup>c</sup>
O(4)	59 (5)	124 (7)	82 (5)	39 (9)	0 <sup>c</sup>	0 <sup>c</sup>
O(5)	91 (6)	54 (4)	71 (4)	6 (8)	0 <sup>c</sup>	0 <sup>c</sup>
Na(1)	79 (3)	77 (3)	62 (2)	61 (5)	0 <sup>c</sup>	0 <sup>c</sup>
Na(2)	64 (3)	66 (3)	66 (2)	22 (4)	0 <sup>c</sup>	0 <sup>c</sup>

<sup>a</sup> Coordinate constrained by symmetry. <sup>b</sup> The form of the anisotropic temperature ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^3 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>c</sup> Value constrained by symmetry.

**Table III.** Interatomic Distances (Å) in Na<sub>2</sub>Fe(CO)<sub>4</sub>·1.5(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) (standard deviations in parentheses)

Distances in the [Fe(CO) <sub>4</sub> ] <sup>2-</sup> anion		Distances in the dioxane molecules	
Fe-C(1)	1.738 (5)	O(3)-C(3)	1.464 (6)
Fe-C(2)	1.745 (6)	C(3)-C(3)	1.507 (8)
C(1)-O(1)	1.175 (7)	O(4)-C(4)	1.453 (7)
C(2)-O(2)	1.162 (8)	O(5)-C(5)	1.449 (7)
		C(4)-C(5)	1.492 (9)
Distances associated with Na(1) <sup>+</sup>		Distances associated with Na(2) <sup>+</sup>	
Na(1)-O(1)'	2.324 (5)	Na(2)-O(3)	2.535 (6)
Na(1)-O(2)	2.318 (5)	Na(2)-O(5)	2.253 (5)
Na(1)-O(3)	2.988 (6)	Na(2)-C(1)	3.050 (5)
Na(1)-O(4)	2.339 (6)	Na(2)-C(1)	2.860 (5)
		Na(2)-Fe	3.086 (2)

**Table IV.** Interatomic Angles (deg) in Na<sub>2</sub>Fe(CO)<sub>4</sub>·1.5(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>) (standard deviations in parentheses)

Angles within the [Fe(CO) <sub>4</sub> ] <sup>2-</sup> Anion <sup>a</sup>			
Fe-C(1)-O(1)	171.0 (4)	Fe-C(2)-O(2)	178.7 (5)
C(1)-Fe-C(1)'	129.7 (2)	O(1)-Fe-O(1)'	136.9 (1)
C(1)-Fe-C(2)	105.5 (2)	O(1)-Fe-O(2)	104.1 (6)
C(2)-Fe-C(2)'	105.6 (3)	O(2)-Fe-O(2)'	105.5 (1)
C(1)-Fe-C(2)'	104.2 (2)	O(1)-Fe-O(2)'	101.6 (1)
Angles around Na(1) <sup>b</sup>			
O(1)-Na(1)-O(1)'	81.1 (2)	O(2)-Na(1)-O(2)'	102.2 (2)
O(1)-Na(1)-O(2)'	164.9 (2)	O(2)-Na(1)-O(3)	81.6 (2)
O(1)-Na(1)-O(2)	87.4 (2)	O(2)-Na(1)-O(4)	100.3 (2)
O(1)-Na(1)-O(3)	88.4 (2)	O(3)-Na(1)-O(4)	176.8 (2)
O(1)-Na(1)-O(4)	89.2 (2)		
Angles around Na(2) <sup>c</sup>			
O(3)-Na(2)-O(5)	89.1 (2)	C(1)-Na(2)-C(1)'	64.3 (2)
O(3)-Na(2)-C(1)'	91.3 (2)	C(1)-Na(2)-(1)'''	109.9 (2)
O(5)-Na(2)-C(1)	92.8 (2)	C(1)-Na(2)-C(1)''	74.1 (1)
O(5)-Na(2)-C(1)'	140.0 (1)	C(1)'-Na(2)-C(1)'''	80.0 (2)
Fe-Na(2)-Fe'	113.2 (1)		
Angles Associated with Dioxane (1) <sup>d</sup>			
Na(1)-O(3)-Na(2)	90.3 (2)	C(3)-O(3)-C(3)''	109.1 (5)
Na(1)-O(3)-C(3)	119.3 (3)	O(3)-C(3)-C(3)'	110.0 (4)
Na(2)-O(3)-C(3)	108.0 (3)		
Angles Associated with Dioxane (2) <sup>c</sup>			
C(4)-O(4)-C(4)'	110.0 (5)	C(4)-C(5)-O(5)	109.6 (5)
C(5)-O(5)-C(5)'	110.3 (4)	Na(1)-O(4)-C(4)	124.6 (3)
O(4)-C(4)-C(5)	109.2 (5)	Na(2)-O(5)-C(5)	124.6 (3)

<sup>a</sup> Refer to Figure 1 for atomic numbering scheme. <sup>b</sup> Refer to Figure 2 for atomic numbering scheme. <sup>c</sup> Refer to Figure 4 for atomic numbering scheme. <sup>d</sup> Refer to Figure 6 for atomic numbering scheme.

counts) + 0.04(net intensity)<sup>2</sup>]<sup>1/2</sup>. The intensities were corrected for Lorentz and polarization effects and were placed on an absolute scale by means of a Wilson plot.<sup>16b</sup>

The coordinates of the iron atom were obtained from a Patterson map and the other non-hydrogen atoms were located from successive difference Fourier maps.<sup>17</sup> Several cycles of isotropic refinement were followed by four cycles of full-matrix anisotropic refinement, resulting in final agreement factors of  $R = 6.1\%$  and  $R_w = 7.8\%$ .<sup>18</sup> A final difference-Fourier map showed no residual peaks larger than 0.6 electron/Å<sup>3</sup>.

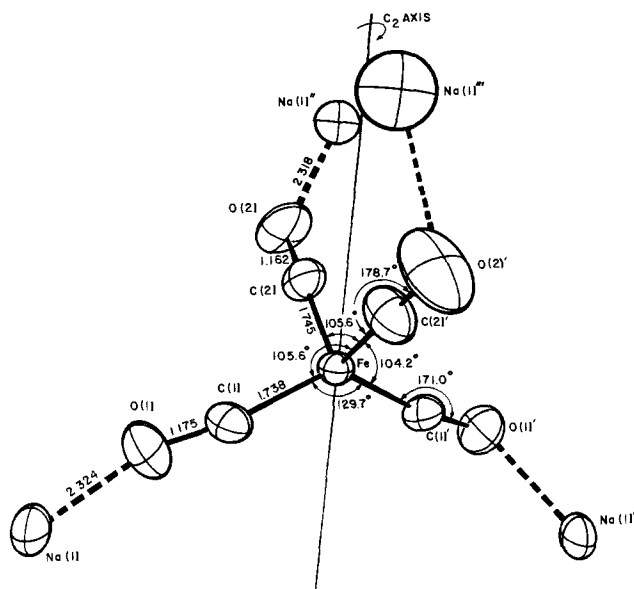
### Description of the Structure

The final atomic parameters are given in Table II, and distances and angles in the molecule are listed in Tables III and IV. A tabulation of observed and calculated structure factors is available.<sup>19</sup> The structure consists of a [Fe(CO)<sub>4</sub>]<sup>2-</sup> anion, two independent Na<sup>+</sup> ions, and one and a half dioxane molecules per asymmetric unit.

**The [Fe(CO)<sub>4</sub>]<sup>2-</sup> Anion.** The [Fe(CO)<sub>4</sub>]<sup>2-</sup> anion (Figure 1) is situated on a crystallographic C<sub>2</sub> rotation axis which

bisects two of the C-Fe-C angles. It is grossly distorted from idealized tetrahedral symmetry, with one angle, C(1)-Fe-C(1)', equal to 129.7 (2)°. The distortion of the C(1)-Fe-C(1)' angle is not reflected in any difference in the iron-carbon distances. The two independent iron-carbon distances are essentially identical, Fe-C(1) = 1.738 (5) Å and Fe-C(2) = 1.745 (6) Å. The other significant distortion found in the dianion is the deviation of the Fe-C(1)-O(1) angle from linearity. The observed Fe-C(1)-O(1) angle of 171.0 (4)° causes the O(1)-Fe-O(1)' angle to be even more distorted (136.9 (1)°) than the C(1)-Fe-C(1)' angle. Each oxygen atom in [Fe(CO)<sub>4</sub>]<sup>2-</sup> is further coordinated to a sodium ion, Na(1). A more subtle and unexpected interaction with the other sodium ion, Na(2), will be described later.

**The Geometry about Na(1)<sup>+</sup>.** Na(1)<sup>+</sup> is situated on a crystallographic mirror plane, and is coordinated to the oxygen atoms of four [Fe(CO)<sub>4</sub>]<sup>2-</sup> groups. The approximately octahedral coordination about Na(1)<sup>+</sup>, Figure 2, is completed by two trans dioxane molecules. The complex pattern of Na(1)<sup>+</sup>...[Fe(CO)<sub>4</sub>]<sup>2-</sup> interactions gives rise to a

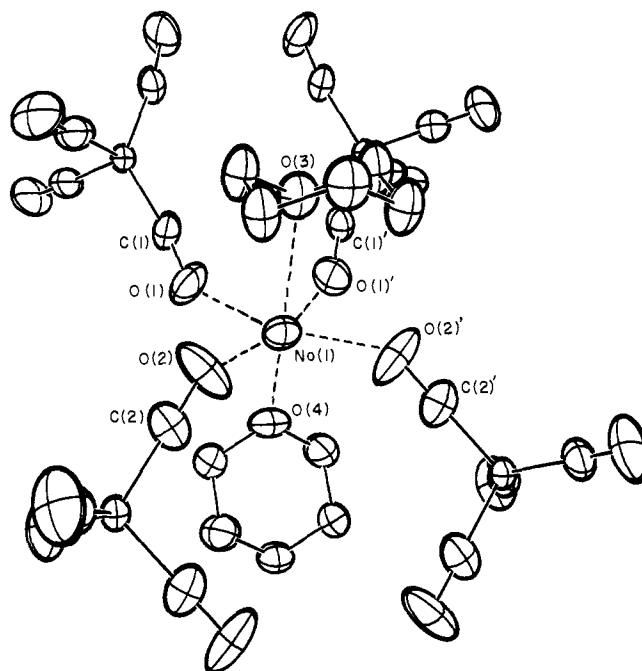


**Figure 1.** A view of the  $[\text{Fe}(\text{CO})_4]^{2-}$  anion, showing the location of the  $C_2$  axis and the arrangement of  $\text{Na}(1)^+$  cations about the carbonyl groups. Note the distortion of the  $\text{C}(1)\text{-Fe-C}(1)'$  angle. 40% probability ellipsoids are used in this diagram, and also in Figures 2, 4, 5, and 6.

three-dimensional “polymeric” network in which each  $[\text{Fe}(\text{CO})_4]^{2-}$  anion is coordinated to four  $\text{Na}(1)^+$  ions and vice versa. A portion of this is shown in the unit cell packing diagram (Figure 3).

**The Geometry about  $\text{Na}(2)^+$ .** The coordination about  $\text{Na}(2)^+$ , which is also situated on a mirror plane, is very intriguing (Figure 4). The only two close contacts to  $\text{Na}(2)^+$  are oxygen atoms from two dioxane molecules ( $\text{Na-O} = 2.253(5)$  and  $2.535(6)$  Å), which make an  $\text{O}(3)\text{-Na}(2)\text{-O}(5)$  angle of  $89.1(2)^\circ$ . The remaining contacts are long-range interactions with the iron and carbon atoms of the  $[\text{Fe}(\text{CO})_4]^{2-}$  anion:  $\text{Na}(2)\cdots\text{C}(1) = 3.050(5)$  Å,  $\text{Na}(2)\cdots\text{C}(1) = 3.050(5)$  Å,  $\text{Na}(2)\cdots\text{Fe} = 3.086(2)$  Å,  $\text{Na}(2)\cdots\text{C}(1)' = 2.860(5)$  Å. The disposition of the  $\text{C}(1)\text{-Fe-C}(1)'$  fragment towards  $\text{Na}(2)^+$  resembles somewhat the coordination of an allyl group towards a transition metal atom. Two  $[\text{Fe}(\text{CO})_4]^{2-}$  anions and two  $\text{Na}(2)^+$  ions come together in such a fashion to form a curious  $(\text{Na}^+)_2[\text{Fe}(\text{CO})_4]^{2-}_2$  “cluster” (Figure 5) with a  $C_2$  axis passing through the iron atoms and a mirror plane perpendicular to it. It is unclear if the forces holding the “cluster” together are sufficiently strong to allow this aggregate to persist in solution (vide infra).

**The Dioxane Molecules.** There are two kinds of dioxane molecules in the unit cell. Dioxane (1), consisting of atoms  $\text{C}(3)$  and  $\text{O}(3)$ , is situated on a site of symmetry  $2/m$  ( $C_{2h}$ ), and dioxane (2), consisting of atoms  $\text{C}(4)$ ,  $\text{C}(5)$ ,  $\text{O}(4)$ , and  $\text{O}(5)$ , is situated on a mirror plane passing through atoms  $\text{O}(4)$  and  $\text{O}(5)$ . Dioxane (1) is somewhat unusual in that its oxygen atoms are each coordinated to two sodium ions (Figure 6). The  $\text{Na}(2)\text{-O}(3)$  distance is normal ( $2.535(6)$  Å) but the  $\text{Na}(1)\text{-O}(3)$  distance of  $2.988(6)$  Å represents the upper-limit of known  $\text{Na}\cdots\text{O}$  interactions.<sup>20</sup> For dioxane (2),  $\text{O}(4)$  is coordinated to  $\text{Na}(1)^+$  while  $\text{O}(5)$  is coordinated to  $\text{Na}(2)^+$ . The average  $\text{Na-O}(\text{carbonyl})$  distance of  $2.321$  Å compares well with the average of the three shorter  $\text{Na-O}(\text{dioxane})$  distance ( $2.376$  Å). These values are in good agreement with the  $\text{Na-O}$  distances found in cryptate and crown ether complexes of  $\text{Na}^+$  where the interatomic distances range from  $2.35$  to  $2.97$  Å.<sup>20</sup>



**Figure 2.** The coordination about  $\text{Na}(1)^+$ . Oxygen atoms from four different  $[\text{Fe}(\text{CO})_4]^{2-}$  groups and two dioxane molecules make up an approximately octahedral coordination sphere about  $\text{Na}(1)^+$ . A mirror plane bisects the  $\text{O}(1)\text{-Na}(1)\text{-O}(1)'$  and  $\text{O}(2)\text{-Na}(1)\text{-O}(2)'$  angles and passes through  $\text{Na}(1)$ ,  $\text{O}(3)$ , and  $\text{O}(4)$ .

### Discussion of the Structure

The crystal structure of  $\text{Na}_2\text{Fe}(\text{CO})_4$  clearly shows the association of a sodium ion  $[\text{Na}(1)]^+$  with carbonyl oxygen atoms, but more significantly it suggests that the second sodium ion  $[\text{Na}(2)]^+$  is also involved in some manner of association with the  $[\text{Fe}(\text{CO})_4]^{2-}$  dianion. The nature of the  $\text{Na}(2)^+\cdots[\text{Fe}(\text{CO})_4]^{2-}$  interaction is novel and not easily rationalized.

The most obvious feature of the  $[\text{Fe}(\text{CO})_4]^{2-}$  geometry is the unusually large value of the  $\text{C}(1)\text{-Fe-C}(1)'$  angle [ $129.7(2)^\circ$ ], in marked contrast to the other  $\text{C-Fe-C}$  angles which are almost tetrahedral. The distortion of the  $\text{C}(1)\text{-Fe-C}(1)'$  and  $\text{O}(1)\text{-Fe-O}(1)'$  angles can be appreciated by examining the 12-atom cyclic fragment shown in Figure 7, which is approximately planar. It is clear that the  $\text{C-Fe-C}$  angle cannot assume a normal tetrahedral value without causing either a decrease in the  $\text{O}\cdots\text{O}$  contact distance or an increase in the  $\text{Fe}\cdots\text{Fe}$  separation. The  $\text{O}\cdots\text{O}$  separations are already at normal van der Waals contact distances ( $3.02$  Å) and cannot be decreased much further. Thus the  $\text{C}(1)\text{-Fe-C}(1)'$  distortion is being maintained by some factor which is preventing the  $\text{Fe}\cdots\text{Fe}$  distance from increasing beyond its current value. This factor appears to be the attractive influence of the  $\text{Na}(2)^+$  ion.

The idea that significant bonding interactions are taking place between  $\text{Na}(2)^+$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  is supported by the geometry about  $\text{Na}(2)^+$  and by the observed  $\text{Na}\cdots\text{C}$  and  $\text{Na}\cdots\text{Fe}$  distances.  $\text{Na}(2)^+$  makes only two short contacts, to dioxane oxygens  $\text{O}(3)$  and  $\text{O}(5)$ . These two atoms define an  $\text{O-Na-O}$  angle of  $89.1(2)^\circ$ , leaving a large “exposed” portion of the  $\text{Na}(2)^+$  coordination sphere not associated with the dioxane molecules. This “exposed region” is oriented towards the  $\text{C-Fe-C}$  moieties of two  $[\text{Fe}(\text{CO})_4]^{2-}$  ions (Figure 4), strongly implying that interactions exist between  $\text{Na}(2)^+$  and the  $\text{C-Fe-C}$  fragments.

The  $\text{Na}(2)\cdots\text{C}(\text{carbonyl})$  distances ( $2.860(5)$  and  $3.050(5)$  Å) and the  $\text{Na}(2)\cdots\text{Fe}$  distance ( $3.086(2)$  Å) in  $\text{Na}_2\text{Fe}(\text{CO})_4$  agree quite well with those found in other com-

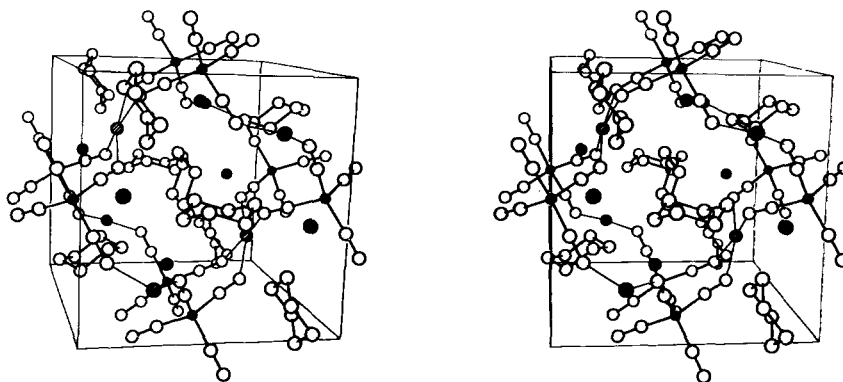


Figure 3. A stereoscopic picture of the unit cell of  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5(\text{dioxane})$  viewed approximately down the  $c$  axis.  $\text{Na}(1)^+$  ions are represented by shaded circles while  $\text{Na}(2)^+$  ions are drawn as cross-hatched circles.

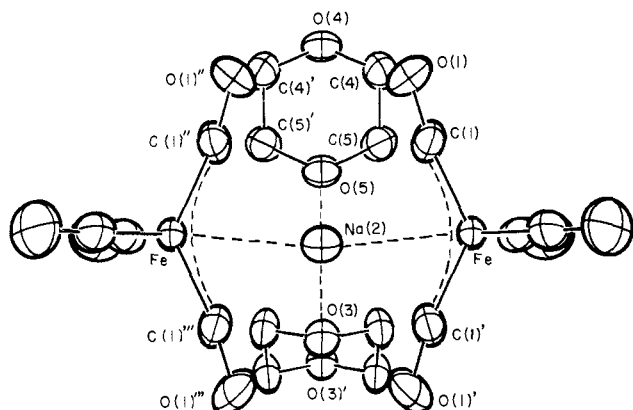


Figure 4. The coordination about  $\text{Na}(2)^+$ . The dioxane molecules are below the plane of the diagram and the two  $[\text{Fe}(\text{CO})_4]^{2-}$  groups are above the plane of the diagram. A mirror plane passes through the center of the figure. The atoms  $\text{O}(3)$ ,  $\text{O}(5)$ ,  $\text{C}(1)$ ,  $\text{C}(1)'$ ,  $\text{C}(1)''$ , and  $\text{C}(1)'''$  define an approximate trigonal prism around  $\text{Na}(2)^+$ .  $\text{Na}(2)^+$  makes two short contacts with the  $\text{O}(3)$  and  $\text{O}(5)$  atoms and longer contacts with the  $\text{C}$  and  $\text{Fe}$  atoms of the anion. The  $\text{Na}(2)^+ \cdots \text{C}-\text{Fe}-\text{C}$  interaction shown here was unanticipated and is most probably responsible for the distortion of the  $\text{C}(1)-\text{Fe}-\text{C}(1)'$  angle.

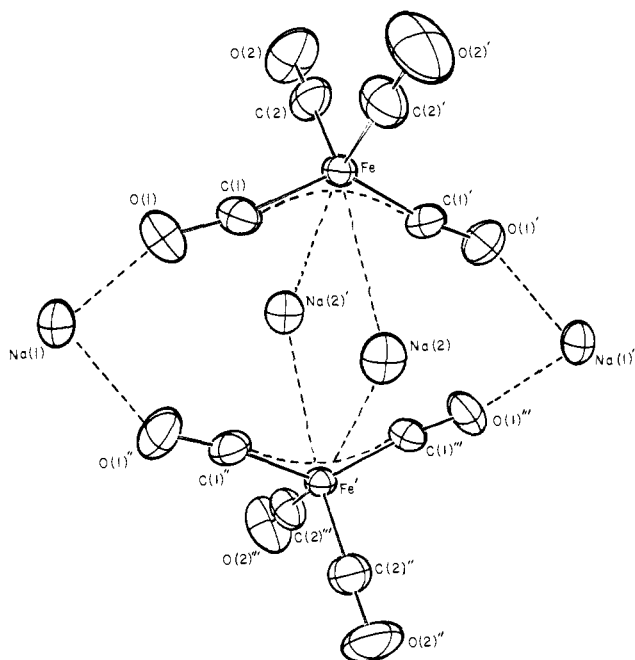


Figure 5. The loosely held "cluster" consisting of two  $[\text{Fe}(\text{CO})_4]^{2-}$  ions and two  $\text{Na}(2)^+$  ions. A twofold rotation axis passes through the iron atoms and a mirror plane passes through the four sodium atoms.  $\text{Na}(2)^+$  makes distances of 3.050 (5), 3.086 (2), and 2.860 (5) Å with  $\text{C}(1)$ ,  $\text{Fe}$ , and  $\text{C}(1)'$ , respectively.

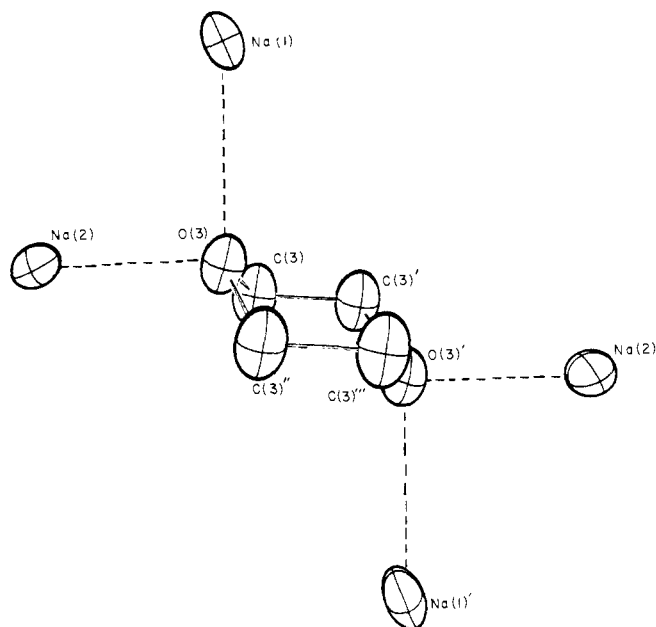


Figure 6. The coordination about dioxane(1). A mirror plane passes through the oxygen and sodium atoms, and a twofold rotation axis passes through the centers of the  $\text{C}-\text{C}$  bonds.

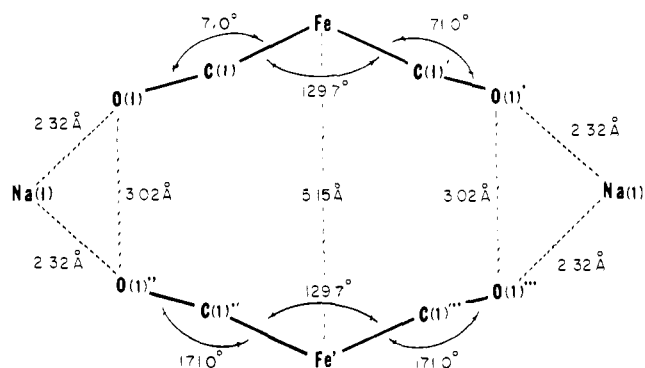


Figure 7. A schematic sketch of the approximately planar portion of the  $(\text{Na}^+)_2[\text{Fe}(\text{CO})_4]^{2-}$  "cluster".  $\text{Na}(2)$  is situated above the plane of the paper, directly over the center of this diagram;  $\text{Na}(2)'$  is similarly situated below the diagram.

pounds where weak sodium-carbon and sodium-transition metal interactions are believed to exist. In the compounds  $[\text{Na}(\text{C}_4\text{H}_8\text{O})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]^{21}$  and  $[\text{Ph}(\text{Na}\cdot\text{OEt})_2(\text{Ph}_2\text{Ni})_2\text{N}_2\text{NaLi}_6(\text{OEt})_4\cdot\text{OEt}_2]^{22}$   $\text{Na}\cdots\text{C}$  distances ranging from 2.74 to 2.96 Å are found for sodium ions associated with the  $\pi$ -electrons of aromatic rings. The  $\text{Na}(2)\cdots\text{Fe}$  distance in  $\text{Na}_2\text{Fe}(\text{CO})_4^{23}$  compares favorably with

Na...Ni distances found recently in several unusual Ni-alkali metal complexes. In  $[\text{Ph}_2\text{NiCH}_2\text{CH}_2]_2\text{Na}_4(\text{THF})_5^{24}$  and  $[\text{Ph}(\text{Na}\cdot\text{OEt})_2(\text{Ph}_2\text{Ni})_2\text{N}_2\text{NaLi}_6(\text{OEt})_4\cdot\text{OEt}]_2^{22}$  Na...Ni distances ranging from 2.80 to 3.12 Å were observed.

The existence of the  $(\text{Na}^+)_2[\text{Fe}(\text{CO})_4]^{2-}$  "clusters" and the distortion of the C-Fe-C angle are thus interrelated features, arising from the unanticipated interaction between  $\text{Na}(2)^+$  and the C-Fe-C portion of the anion. It is uncertain if the  $(\text{Na}^+)_2[\text{Fe}(\text{CO})_4]^{2-}$  "clusters" found here represent an actual chemical species (transient, perhaps) that might exist in solution or are artifacts of crystal packing. The important point is that the geometry of the  $\text{Na}(2)^+\cdots\text{C-Fe-C}$  region in this crystal structure gives one the rare opportunity of studying at a detailed level the geometric changes that take place in  $[\text{Fe}(\text{CO})_4]^{2-}$  when  $\text{Na}^+$  is in close proximity, and allows us to speculate on events that might occur in solution when  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $\text{Na}^+$  are brought into contact. One could imagine a situation in which  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $\text{Na}^+$  ions are initially attracted to each other by electrostatic forces. The close approach of the positively charged sodium ion might then induce a distortion of the normally spherical arrangement of nonbonding electrons on the iron atom and impart some directional character to the nonbonding electron density. The subsequent redistribution of electron density could then result in a distortion of the original tetrahedral geometry<sup>25</sup> and the establishment of "lone pairs" of electrons directed at  $\text{Na}^+$ .

It is likely, then, that ion pairing between  $\text{Na}^+$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  in solution would result in significant distortion of the  $[\text{Fe}(\text{CO})_4]^{2-}$  geometry, with the magnitude of distortion probably dependent on the charge density of the cationic species. When  $\text{Na}^+$  ions are isolated from  $[\text{Fe}(\text{CO})_4]^{2-}$ , as in the solid-state structure of  $[\text{Na}(\text{cryptate})]_2^+[\text{Fe}(\text{CO})_4]^{2-}$  (cryptate =  $\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{N}$ ), the  $[\text{Fe}(\text{CO})_4]^{2-}$  anion shows an undistorted tetrahedral structure.<sup>29</sup>

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**Supplementary Material Available:** a listing of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) Alfred P. Sloan Fellow, 1974-1976.
- (2) J. P. Collman, *Acc. Chem. Res.*, in press.
- (3) (a) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972); (b) J. N. Cawse, Ph.D. Dissertation, Stanford University, 1973.
- (4) (a) M. P. Cooke, *J. Am. Chem. Soc.*, **92**, 6080 (1970); (b) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972); (c) W. O. Siegl and J. P. Collman, *ibid.*, **94**, 2516 (1972); (d) J. P. Collman, S. R. Winter, and R. G. Komoto, *ibid.*, **95**, 249 (1973); (e) J. P. Collman, R. G. Komoto, and W. O. Siegl, *ibid.*, **95**, 2389 (1973); (f) J. P. Collman and N. W. Hoffman, *ibid.*, **95**, 2689 (1973).
- (5) (a) Y. Takegami, Y. Watanabe, I. Kanada, T. Mitsudo, T. Okajima, Y. Morishita, and H. Masada, *Bull. Chem. Soc. Jpn.*, **41**, 2990 (1968); (b) Y. Takegami, Y. Watanabe, and H. Masada, *ibid.*, **40**, 1456 (1967).
- (6) (a) R. G. Komoto, Ph.D. Dissertation, Stanford University, 1974; (b) J. P. Collman and R. G. Komoto, U.S. Patent Application filed June 11, 1973.
- (7) (a) H. Masada, M. Mizuno, S. Suza, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **43**, 3824 (1970); (b) Y. Watanabe, T. Mitsudo, M. Tanaka, K. Yamamoto, T. Okajima, and Y. Takegami, *ibid.*, **44**, 2569 (1971).
- (8) (a) W. F. Edgell, J. Lyford, A. Barbetta, and C. J. Jose, *J. Am. Chem. Soc.*, **93**, 6403 (1971); (b) W. F. Edgell and L. Lyford, *ibid.*, **6407** (1971).
- (9) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).
- (10) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).
- (11) J. Chiang, M.S. Thesis, University of Southern California, 1974.
- (12) J. M. Burlitch, S. W. Ulmer, J. J. Stezowski, R. C. Winterton, R. Eiss, and R. E. Hughes, Abstracts of the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 1973, p 140.
- (13) D. P. Schussler, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, **13**, 153 (1974).
- (14) The crystals used in this work were obtained directly from a sample purchased from Alfa Inorganics, Ventron Corp., Beverly, Mass.
- (15) T. C. Furnas, "Single Crystal Orienter Manual", General Electric Co., Milwaukee, Wisc., 1966.
- (16) (a) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); (b) H. A. Levy et al., Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Sept 1970, p 135 ff.
- (17) The major computations in this work were performed on the USC IBM 370-155 computer using CRYM, an amalgamated set of crystallographic programs developed by Dr. Richard Marsh's group at the California Institute of Technology.
- (18)  $R = \sum |F_o - |F_d|| / \sum F_o$ ;  $R_w = \{ \sum w |F_o - |F_d||^2 / \sum w F_o^2 \}^{1/2}$
- (19) See paragraph at the end of this paper for details.
- (20) M. RQ/Truter, *Struct. Bonding (Berlin)*, **16**, 71 (1973)
- (21) D. J. Brauer and G. D. Stucky, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
- (22) K. Jonas, D. J. Brauer, C. Krüger, P. J. Roberts, and Y. H. Tsay, *J. Am. Chem. Soc.*, **98**, 74 (1976).
- (23) It is rather difficult to evaluate the true significance of the Na...Fe distance because of the lack of suitable standards for comparison. The Fe-Mg  $\sigma$ -bonded distance of 2.59 Å found in  $(\pi\text{-C}_5\text{H}_5)(\text{diphos})\text{FeMgBr}\cdot 3\text{THF}$  (H. Felkin et al., *J. Chem. Soc., Chem. Commun.*, **44** (1974)) would predict a Fe-Na  $\sigma$ -bond length of 2.83 Å when the differences in covalent radii between Mg and Na are taken into account. It is questionable, however, if this could be used to evaluate distances involving sodium ions.
- (24) D. J. Brauer, C. Krüger, P. J. Roberts, and Y. H. Tsay, submitted for publication.
- (25) Another point worth considering is that a  $[\text{CO}]^-$  group is formally iso-electronic with a nitrosyl group. It has been noticed<sup>28</sup> that the trend  $\text{OC-M-CO} < \text{ON-M-CO} < \text{ON-M-NO}$  is often observed in L-M-L bond angles:  $\text{ON-M-NO}$  angles as large as 154.2 and 167° have been found in formally tetrahedral iridium complexes.<sup>27,28</sup> Interestingly, these distortions are often found coupled to distortions of the M-N-O angle from linearity. The trend  $\text{OC-M-CO} < \text{ON-M-CO} < \text{ON-M-NO}$  has been attributed to a larger charge density on nitrogen relative to carbon, causing the nonbonded radius for nitrogen to be larger than that for carbon.<sup>26</sup> An alternative explanation for the distortion of the C(1)-Fe-C(1') angle in  $\text{Na}_2\text{Fe}(\text{CO})_4$  could thus be obtained by postulating that the two negative charges are largely localized on the C(1)O(1) and C(1')O(1') groups, causing (i) larger nonbonded radii for these carbon atoms relative to C(2)O(2) and C(2')O(2'), (ii) increased electron-electron repulsion between C(1)O(1) and C(1')O(1'), and (iii) a greater affinity for  $\text{Na}^+$  ions. We feel, however, that this explanation is less satisfactory than the one given in the text because it would predict significant differences between the Fe-C(1) and Fe-C(2) bond lengths, differences not observed experimentally.
- (26) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2812 (1972).
- (27) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).
- (28) M. Angoletta, G. Ciani, M. Manassero, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 789 (1973).
- (29) R. G. Teller, H. B. Chin, and R. Bau, unpublished results.