to FePc. The N_p–C_a bonds in ZnPc decrease in length, while the C_a–N_m and C_b–C_b bonds lengthen. The radial expansion of the core leads to increased C_a–N_p–C_a and C_a–N_m–C_a bond angles and a decreased N_p–C_a–C_b bond angle. The observed changes, although relatively small (especially the bond length differences), are exactly the same type of skeletal parameter changes observed in accommodating radial expansion of the porphinato core.[28]

The pattern of intermolecular contacts in ZnPc are similar to those reported for other β-polymorph phthalocyanine derivatives.[5,12] The contact between the zinc atom and the aza-methine nitrogen atom N(1) is 3.23 Å. The N(1)ZnN(4) angle is 84.4°; N(1)ZnN(2) is 89.0°. The deviation of N(1) from the mean plane (Figure 1) is toward the zinc atom of an adjacent molecule. This type of M···N(1) "interaction" has been suggested to stabilize the β-polymorph crystal structure.[12]

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Supplementary Material Available: Table II, anisotropic thermal parameters, and listings of structure factor amplitudes (× 10) (21 pages). Ordering information is given on any current masthead page.

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Dependence of the $[Fe(CO)_4]^{2-}$ Geometry on Counterion: Crystal Structures of $K_2Fe(CO)_4$ and $[Na(crypt)]_2[Fe(CO)_4]$ [crypt = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$]

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Abstract: In marked contrast to the highly distorted $[Fe(CO)_4]^{2-}$ anion found in $Na_2Fe(CO)_4 \cdot 1.5$(dioxane) (C–Fe–C = 129.7°), the $[Fe(CO)_4]^{2-}$ ion in $[Na(crypt)]_2[Fe(CO)_4]$ [crypt = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$] has essentially undistorted tetrahedral symmetry. In $K_2Fe(CO)_4$, the $[Fe(CO)_4]^{2-}$ ion shows an intermediate amount of distortion (C–Fe–C = 121.0°). It is suggested that this trend reflects the decreasing charge density along the series Na^+, K^+, $Na(crypt)^+$, and reinforces the belief that distortions in $[Fe(CO)_4]^{2-}$ are triggered by the presence of highly charged species in close proximity. Crystallographic details: $K_2Fe(CO)_4$, space group *Fddd* (orthorhombic), $a = 23.072$ (6), $b = 11.557$ (2), $c = 5.543$ (1) Å, $V = 1478$ Å^3, $Z = 8$; $R = 4.9\%$ for 386 nonzero reflections; $[Na(crypt)]_2[Fe(CO)_4]$, space group $P2_12_12_1$ (orthorhombic), $a = 16.360$ (3), $b = 12.592$ (2), $c = 23.058$ (6) Å, $V = 4750$ Å^3, $Z = 4$; $R = 9.3\%$ for 2158 nonzero reflections.

Introduction

The behavior of the alkali metal salts of metal carbonylate ions in solution has attracted considerable attention. Edgell,[2] Brown,[3a] Darensbourg,[3b] and their co-workers have demonstrated the existence of contact ion pairs or solvent-separated ion pairs in solutions of $[Co(CO)_4]^-$ and $[Mn(CO)_5]^-$, and very recently Pannell and Jackson[3c] have implicated the existence of direct Na–Fe interactions in solutions of Na[$Fe(CO)_2(C_5H_5)$]. Contact ion pairs are commonly found in solutions of relatively poorly coordinating solvents such as tetrahydrofuran (THF): here direct cation–anion interaction causes a distinct lowering of symmetry of the anion, such as T_d to C_{3v} in the case of $[Co(CO)_4]^-$. In more highly coordinating solvents such as hexamethylphosphoric triamide (HMPA), on the other hand, the full symmetry of the metal carbonylate anion is expressed, presumably because the cation is now surrounded by solvent molecules and unavailable to interact directly with the anion. Nevertheless, even in this latter case conductivity measurements still show evidence of considerable ion pairing, and this has been interpreted to support the existence of solvent-separated ion pairs.

Recently, we reported the dramatic effect of ion pairing upon the alkyl migration reactions of $[RFe(CO)_4]^-$,[4a] and have shown that the rates of alkyl halide S_N2 ozidative additions to $Na_2Fe(CO)_4$ are extremely solvent dependent.[4c] In *N*-methylpyrrolidinone (NMP), $Na_2Fe(CO)_4$ exists and reacts predominately as the highly nucleophilic solvent-separated complex, $[Na;S:Fe(CO)_4]^-$ (S = solvent), and free Na^+, but not as dissociated $[Fe(CO)_4]^{2-}$. In THF, the less reactive ion pair, $Na_2Fe(CO)_4$, is the dominant solution species.[4c]

Because of the dramatic effect of ion pairing upon the solution chemistry of $Na_2Fe(CO)_4$, we decided to investigate the solid state structures of a series of $[Fe(CO)_4]^{2-}$ salts, with the hope of elucidating possible $[Fe(CO)_4]^{2-}$ cation binding sites and to see whether cation-induced distortions of the $[Fe(CO)_4]^{2-}$ unit occur in the solid state.

In our recent structure determination of $Na_2Fe(CO)_4 \cdot 1.5(dioxane)$[5] we found that the geometry of $[Fe(CO)_4]^{2-}$ was indeed influenced by the presence of the Na^+ ions. In that structure determination a highly distorted C–Fe–C angle (129.7°) was found, coupled to a curious association of one of the Na^+ with the C–Fe–C portion of the anion (almost as in a π-allylic type configuration). In this paper, we describe the effects of (a) changing the cation to one of a lower charge density (K^+), and (b) removing the Na^+ ion from the sphere of influence of $[Fe(CO)_4]^{2-}$ by the use of a cryptand chelator, $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ (hereafter designated "crypt").

Experimental Section

The detailed preparations of $Na_2Fe(CO)_4$ and $K_2Fe(CO)_4$ have been described elsewhere.[4c] Since these compounds are air and moisture sensitive, all preparations were carried out under nitrogen. Crystallizations were performed in a Vac-Atmospheres inert atmosphere (nitrogen) drybox. Solvents were dried and deoxygenated in the following manner. *N*-Methylpyrrolidinone (NMP) was distilled from CaH_2 under reduced pressure. CH_3OH and THF were distilled from $Mg(OCH_3)_2$ and Na/benzophenone, respectively, under nitrogen.

After the addition of 2 equiv of cryptate (Kryptofix 222, purchased from E. M. Merck), crystallization of $[Na(crypt)]_2[Fe(CO)_4]$ from THF/NMP by THF vapor diffusion afforded colorless prisms. $K_2Fe(CO)_4$ was crystallized as light-gold needles from THF/CH_3OH by THF vapor diffusion.

Data Collection. The general method of data collection was the same for both compounds. A specimen was mounted (in a glass capillary) under an inert atmosphere and preliminary photographs revealed the space groups of each. The unit cell parameters (listed in Table I together with other relevant crystal data) were found by a least-squares fit of several carefully measured angle settings on a Nonius CAD-3 automated diffractometer.

Data were collected with Zr-filtered Mo Kα radiation in the θ–2θ scan mode. A scan speed of 10°/min was used with the scan defined as $\Delta\theta = (1.2 + 0.15 \tan \theta)°$. Each scan was taken between two and eight times with background counts taken at the beginning and at the end of each scan. Zirconium attenuators were used to prevent the counting rate from exceeding 2500 counts/s. Three check reflections were monitored every 50 reflections during data collection as a check on the stability of the crystals and diffractometer. Examination of the check reflections revealed no decay of the crystals. Empirical absorption corrections were applied to each data set and were based on the variation of intensity of an axial (χ = 90°) reflection as a function of spindle angle ϕ.[6a]

Table I. Crystal Data for $K_2Fe(CO)_4$ and $[Na(crypt)]_2[Fe(CO)_4]$

	$K_2Fe(CO)_4$	$[Na(crypt)]_2[Fe(CO)_4]$
Crystal type	Orthorhombic	Orthorhombic
Space Group	*Fddd* (No. 70)	$P2_12_12_1$ (No. 19)
Cell constants: *a*	23.072 (6) Å	16.360 (3) Å
b	11.557 (2) Å	12.592 (2) Å
c	5.543 (1) Å	23.058 (6) Å
Cell volume	1478 Å^3	4750 Å^3
No. of molecules in the unit cell	8	4
Calcd density	2.21 g cm^{-3}	1.35 g cm^{-3}
Obsd density		1.33 g cm^{-3}
Absorption coefficient (μ) for Mo Kα x rays	31.4 cm^{-1}	4.20 cm^{-1}
Variation in transmission coefficient (normalized to an average of unity)	0.82–1.13	0.98–1.02
Data collected and merged	2 octants	2 octants
2θ upper limit used in data collection	55°	45°
Reflections used in the structure analysis	386	2158
Final agreement factor	R = 4.9%	R = 9.3%

Intensities greater than 3σ (σ = one standard deviation) were retained for the subsequent structure analysis. The standard deviation of each intensity was calculated using the expression

$$\sigma(I) = [I_{\text{peak}} + I_{\text{background}} + (0.04 I_{\text{peak}})^2]^{1/2}$$

The intensities were corrected for Lorentz and polarization effects and placed on an absolute scale by means of a Wilson plot.[6b]

Structure Analysis. For $K_2Fe(CO)_4$ space group requirements (*Fddd*; Z = 8) uniquely placed the Fe atom at 0.125, 0.125, 0.125 (site symmetry D_2) and the potassium atom position was located from the Patterson map. The carbon and oxygen atoms were located from a subsequent difference Fourier map. Five cycles of full-matrix least-squares refinement[6b] resulted in final R factors[7] of R = 4.9% and R_w = 6.4% for 386 nonzero reflections, with all atoms anisotropic.

For $[Na(crypt)]_2Fe(CO)_4$ the iron atom position was located from a Patterson map, and all other nonhydrogen atoms slowly added through a succession of structure factor calculations followed by difference Fourier maps. During the structure solution of this com-

Table II. Final Atomic Parameters in $K_2Fe(CO)_4$[c]

(A) Atomic Positions (in fractional coordinates)

Atom	*x*	*y*	*z*
Fe	0.1250[a]	0.1250[a]	0.1250[a]
K	0.4477 (1)	0.1250[a]	0.1250[a]
C	0.4200 (2)	0.4493 (3)	0.0755 (6)
O	0.4496 (2)	0.4951 (3)	0.2184 (6)

(B) Thermal Parameters[b] (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	10 (1)	39 (1)	156 (4)	0 (0)[a]	0 (0)[a]	0 (0)[a]
K	16 (1)	51 (1)	242 (5)	0 (0)[a]	0 (0)[a]	−24 (3)
C	13 (1)	48 (2)	194 (10)	−2 (2)	−1 (4)	−2 (9)
O	22 (1)	70 (3)	239 (11)	−18 (2)	−34 (5)	−33 (8)

[a] Value fixed by crystal symmetry. [b] The form of the anisotropic temperature ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^3 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c] Standard deviations in parentheses.

Table III. Final Atomic Parameters in $[Na(crypt)]_2[Fe(CO)_4]$[b]

(A) Atomic Positions (in fractional coordinates)

Atom	x	y	z	Atom	x	y	z
Fe(1)	0.2521 (2)	0.2294 (2)	0.1695 (1)	C(34)	0.7506 (30)	−0.0002 (22)	0.2059 (13)
C(4)	0.1463 (11)	0.2327 (16)	0.1643 (8)	O(35)	0.7120 (8)	0.1084 (13)	0.2240 (6)
C(5)	0.2973 (11)	0.3339 (17)	0.1263 (9)	C(36)	0.6475 (24)	0.1012 (36)	0.2653 (14)
C(6)	0.2864 (10)	0.1052 (14)	0.1443 (7)	C(37)	0.5774 (18)	0.1518 (21)	0.2520 (11)
C(7)	0.2857 (10)	0.2429 (13)	0.2408 (7)	Na(3)	−0.0304 (4)	0.2361 (5)	0.4481 (3)
O(8)	0.0729 (8)	0.2327 (14)	0.1608 (6)	N(45)	−0.0770 (10)	0.1802 (15)	0.3318 (8)
O(9)	0.3291 (10)	0.3979 (12)	0.1003 (7)	C(46)	−0.1364 (14)	0.2639 (23)	0.3128 (9)
O(10)	0.3152 (8)	0.0280 (11)	0.1304 (6)	C(47)	−0.1870 (16)	0.3107 (20)	0.3634 (11)
O(11)	0.3114 (8)	0.2490 (11)	0.2876 (6)	O(48)	−0.1342 (9)	0.3498 (12)	0.4065 (7)
Na(2)	0.6939 (3)	0.2373 (4)	0.1384 (2)	C(49)	−0.0992 (19)	0.4584 (25)	0.3988 (17)
N(12)	0.8411 (8)	0.2762 (13)	0.0779 (6)	C(50)	−0.0752 (24)	0.4952 (24)	0.4541 (20)
C(13)	0.8819 (12)	0.3698 (20)	0.1066 (10)	O(51)	−0.0082 (10)	0.4287 (11)	0.4729 (7)
C(14)	0.8687 (16)	0.3654 (18)	0.1734 (12)	C(52)	0.0161 (29)	0.4636 (27)	0.5286 (17)
O(15)	0.7886 (9)	0.3669 (11)	0.1891 (5)	C(53)	0.0437 (20)	0.3886 (27)	0.5640 (16)
C(16)	0.7569 (20)	0.4668 (20)	0.1972 (10)	N(54)	0.0192 (11)	0.2772 (18)	0.5619 (8)
C(17)	0.6671 (18)	0.4624 (18)	0.2149 (11)	C(55)	−0.0451 (26)	0.2520 (53)	0.6008 (12)
O(18)	0.6272 (9)	0.4068 (10)	0.1669 (7)	C(56)	−0.1216 (20)	0.2096 (40)	0.5819 (13)
C(19)	0.5411 (16)	0.3934 (22)	0.1708 (17)	O(57)	−0.1344 (8)	0.1846 (13)	0.5291 (7)
C(20)	0.5128 (15)	0.3078 (22)	0.2104 (12)	C(58)	−0.1701 (15)	0.0789 (19)	0.5207 (13)
N(21)	0.5561 (9)	0.2036 (12)	0.2009 (7)	C(59)	−0.1753 (16)	0.0570 (18)	0.4628 (12)
C(22)	0.5076 (16)	0.1270 (25)	0.1679 (17)	O(60)	−0.0981 (10)	0.0553 (10)	0.4375 (7)
C(23)	0.5020 (15)	0.1395 (24)	0.1117 (15)	C(61)	−0.0898 (19)	0.0082 (21)	0.3846 (15)
O(24)	0.5810 (8)	0.1598 (11)	0.0793 (6)	C(62)	−0.1251 (19)	0.0760 (20)	0.3356 (11)
C(25)	0.5662 (12)	0.2016 (16)	0.0232 (10)	C(63)	−0.0035 (21)	0.1783 (30)	0.2964 (12)
C(26)	0.6454 (13)	0.2346 (17)	0.0009 (8)	C(64)	0.0570 (19)	0.2656 (34)	0.3115 (11)
O(27)	0.6750 (8)	0.3163 (11)	0.0375 (5)	O(65)	0.0826 (9)	0.2676 (13)	0.3703 (6)
C(28)	0.7447 (16)	0.3723 (16)	0.0130 (8)	C(66)	0.1496 (17)	0.2031 (23)	0.3838 (13)
C(29)	0.8234 (13)	0.3055 (16)	0.0163 (8)	C(67)	0.1706 (16)	0.1896 (21)	0.4424 (12)
C(30)	0.8920 (17)	0.1828 (20)	0.0771 (11)	O(68)	0.1020 (10)	0.1561 (13)	0.4734 (7)
C(31)	0.8428 (14)	0.0832 (16)	0.0716 (11)	C(69)	0.1138 (23)	0.1360 (38)	0.5378 (14)
O(32)	0.7819 (7)	0.0701 (9)	0.1187 (6)	C(70)	0.0908 (20)	0.2050 (21)	0.5751 (12)
C(33)	0.8087 (17)	0.0235 (20)	0.1745 (15)				

(B) Thermal Parameters[a] ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	21 (1)	44 (1)	10 (1)	−4 (3)	−1 (1)	−1 (2)
C(4)	27 (8)	99 (16)	23 (5)	−2 (20)	5 (11)	44 (18)
C(5)	34 (8)	80 (16)	16 (5)	10 (20)	5 (11)	11 (15)
C(6)	36 (8)	43 (13)	14 (4)	15 (16)	21 (8)	−14 (11)
C(7)	37 (7)	53 (13)	6 (3)	28 (15)	−8 (7)	4 (11)
O(8)	30 (6)	183 (16)	31 (4)	32 (17)	−2 (8)	25 (15)
O(9)	71 (8)	93 (13)	29 (4)	−32 (18)	−4 (9)	50 (12)
O(10)	56 (7)	61 (10)	37 (4)	−26 (15)	31 (9)	−56 (11)
O(11)	70 (7)	100 (13)	20 (3)	20 (17)	−18 (8)	−18 (12)
Na(2)	26 (2)	46 (4)	10 (1)	−10 (6)	1 (3)	−6 (4)
N(12)	28 (6)	77 (12)	18 (4)	4 (17)	−7 (7)	4 (12)
C(13)	41 (10)	137 (22)	22 (6)	−46 (24)	−9 (13)	−8 (18)
C(14)	56 (12)	84 (20)	36 (7)	−26 (24)	−52 (17)	12 (20)
O(15)	48 (7)	66 (11)	21 (3)	−19 (13)	11 (7)	−26 (9)
C(16)	66 (14)	100 (22)	34 (7)	−58 (36)	−5 (18)	−6 (18)
C(17)	64 (14)	97 (20)	34 (7)	22 (30)	28 (17)	−27 (18)
O(18)	55 (7)	68 (11)	33 (4)	−10 (15)	21 (10)	−8 (12)
C(19)	43 (11)	124 (24)	75 (11)	41 (28)	−28 (20)	46 (30)
C(20)	65 (13)	118 (25)	40 (8)	13 (30)	55 (17)	5 (22)
N(21)	31 (6)	66 (14)	23 (4)	−30 (15)	18 (9)	−11 (12)
C(22)	63 (14)	186 (31)	31 (9)	−96 (34)	31 (21)	−17 (31)
C(23)	54 (13)	187 (31)	36 (9)	−131 (32)	16 (18)	−6 (27)
O(24)	39 (6)	97 (11)	20 (3)	−22 (14)	−14 (7)	14 (10)
C(25)	43 (10)	94 (18)	22 (5)	35 (21)	−35 (12)	−11 (16)
C(26)	56 (11)	79 (16)	20 (5)	−27 (24)	−20 (11)	16 (16)
O(27)	35 (6)	88 (11)	15 (3)	11 (14)	−8 (7)	−9 (10)
C(28)	53 (10)	114 (17)	17 (4)	−8 (31)	−2 (14)	41 (14)
C(29)	53 (10)	94 (18)	13 (4)	29 (22)	4 (10)	25 (13)
C(30)	80 (15)	81 (21)	31 (7)	0 (33)	22 (16)	−12 (19)
C(31)	47 (11)	70 (17)	46 (8)	21 (24)	−6 (15)	−46 (18)
O(32)	29 (5)	75 (10)	22 (3)	3 (11)	−6 (7)	4 (9)
C(33)	65 (15)	88 (21)	44 (10)	37 (29)	−45 (21)	0 (24)
C(34)	113 (20)	107 (23)	30 (8)	−92 (45)	−17 (26)	69 (21)
O(35)	42 (6)	114 (14)	26 (4)	6 (15)	11 (8)	47 (11)

Table III *(Continued)*

			(B) Thermal Parameters[a] ($\times 10^4$)			
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(36)	91 (20)	350 (56)	32 (9)	100 (58)	61 (22)	148 (38)
C(37)	66 (15)	123 (24)	28 (7)	28 (30)	35 (16)	46 (20)
Na(3)	30 (3)	48 (5)	13 (1)	3 (6)	−2 (3)	5 (5)
N(45)	47 (8)	125 (16)	16 (4)	3 (20)	9 (10)	−14 (14)
C(46)	58 (10)	183 (26)	13 (5)	64 (32)	−11 (11)	−4 (19)
C(47)	78 (13)	135 (24)	27 (6)	35 (30)	5 (17)	6 (20)
O(48)	54 (7)	85 (13)	33 (4)	39 (15)	−45 (10)	−11 (12)
C(49)	80 (16)	94 (25)	61 (12)	83 (33)	−15 (23)	40 (27)
C(50)	93 (22)	108 (26)	59 (12)	−51 (42)	26 (27)	−38 (29)
O(51)	67 (8)	62 (10)	17 (4)	−33 (16)	−7 (8)	−1 (10)
C(52)	150 (29)	118 (29)	32 (10)	−160 (52)	18 (26)	15 (29)
C(53)	119 (20)	91 (26)	46 (10)	−2 (38)	−89 (23)	−63 (27)
N(54)	46 (9)	136 (20)	21 (5)	0 (23)	−5 (10)	−23 (16)
C(55)	110 (23)	542 (74)	20 (8)	22 (85)	9 (21)	80 (44)
C(56)	79 (17)	441 (74)	15 (7)	−170 (60)	−6 (18)	−78 (36)
O(57)	44 (7)	153 (17)	23 (4)	−65 (17)	16 (9)	−24 (12)
C(58)	60 (12)	94 (19)	36 (8)	−24 (26)	34 (16)	47 (20)
C(59)	71 (14)	84 (20)	28 (7)	−46 (26)	10 (15)	3 (18)
O(60)	62 (9)	47 (10)	30 (4)	5 (14)	−2 (10)	−2 (10)
C(61)	99 (17)	94 (22)	42 (9)	−8 (33)	−34 (20)	−35 (25)
C(62)	116 (18)	104 (21)	28 (7)	−27 (33)	−49 (19)	−45 (21)
C(63)	81 (19)	221 (38)	27 (7)	53 (47)	−33 (20)	−22 (26)
C(64)	86 (17)	266 (44)	14 (6)	−133 (53)	21 (15)	26 (26)
O(65)	56 (7)	120 (13)	20 (4)	−11 (18)	15 (8)	−22 (13)
C(66)	70 (13)	180 (32)	32 (8)	122 (36)	48 (17)	36 (25)
C(67)	62 (13)	162 (28)	24 (6)	44 (31)	−15 (16)	32 (22)
O(68)	54 (8)	140 (15)	28 (4)	65 (18)	18 (10)	44 (13)
C(69)	153 (26)	308 (50)	24 (8)	347 (63)	40 (22)	86 (33)
C(70)	119 (18)	114 (25)	23 (7)	89 (35)	−35 (18)	−7 (20)

[a] The form of the anisotropic temperature ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^3 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Standard deviations in parentheses.

Table IV. Distances and Angles in $K_2Fe(CO)_4$[b]

Distances (Å) in the $[Fe(CO)_4]^{2-}$ Anion (see Figure 1)			
Fe–C	1.746 (4)	K–O	3.615 (4)
C–O	1.175 (5)	K–C′	3.401 (4)
K–Fe	3.617 (1)	K–O′	3.804 (4)
K–C	3.280 (3)		
Distances (Å) Near K^+ (see Figure 3)			
K–O*	2.709 (3)	K–Fe	3.617 (1)
K–O**	2.876 (4)	K–C′	3.401 (4)
K–C	3.280 (3)		
Angles in the $[Fe(CO)_4]^{2-}$ Anion (see Figure 1)			
Fe–C–O	176.6 (3)°	C–Fe–C″	107.1 (2)°
C–Fe–C′	121.0 (2)°	C–Fe–C‴	101.0 (2)°
Angles Involving K^+ (see Figure 3)			
O*–K–O*	178.0 (1)°	C–K–C′	54.1 (1)°
O*–K–O**	90.1 (1)°, 88.3 (1)°	Fe–K–Fe	124.7 (1)°
O**–K–O**	69.4 (1)°		
Nonbonding Contact Distances (Å)			
O···O ($x, \frac{5}{4} - y, \frac{1}{4} - z$)			3.175 (5)
O···O ($x, \frac{3}{4} - y, \frac{3}{4} - z$)			3.276 (5)[a]
O···O ($1 - x, 1 - y, -z$)			3.352 (5)

[a] Shown as O**···O** in Figure 3. [b] Standard deviations in parentheses.

pound the locations of some of the ethylene groups were ambiguous, the first evidence of possible disorder in the cryptate molecules. After all atoms were located, six cycles of full-matrix least-squares refinement[6b] with all atoms treated anisotropically resulted in final agreement factors of R = 9.3%, R_w = 9.2%.[7] A final difference Fourier revealed no peaks larger than 0.4 e/Å^3.

Description of the Structures

Final atomic parameters for the two structures are given in Tables II and III, and important distances and angles are summarized in Tables IV and V. Listings of the observed and calculated structure factors are available.[8]

Structure of $K_2Fe(CO)_4$. The structure of the complex can be viewed as discrete $[Fe(CO)_4]^{2-}$ fragments held together by a network of K^+···O interactions.

The $Fe(CO)_4$ anion (Figure 1) is crystallographically constrained to 222 (D_2) symmetry, with the three mutually perpendicular C_2 axes bisecting pairs of C–Fe–C angles. Thus there are only three unique C–Fe–C angles and one unique value for each of the Fe–C and C–O distances (Table IV). The Fe–C–O fragment is essentially linear and the Fe–C and C–O distances are similar to those found in other iron carbonyl complexes. The interesting feature in $K_2Fe(CO)_4$ is an unusual C–Fe–C bond angle of 121.0° subtended by two potassium atoms. The closest approach of K^+ to the C–Fe–C fragment is to the carbon atoms (see Table IV). This interaction and the resultant distortion of the "expected" tetrahedral geometry will be discussed later.

The K^+ ion is located on a crystallographic twofold axis, which means that all interactions of K^+ with other atoms come in symmetry-related pairs. The distances of closest approach are: K–O = 2.71, 2.88; K–C = 3.28, 3.40; and K–Fe = 3.62 Å (Figures 2 and 3). The exact coordination about K^+ is difficult to define, as there are eight atoms within 3.4 Å of K^+, 14 within 3.6 Å, and 20 within 3.8 Å.

Structure of $[Na(crypt)]_2Fe(CO)_4$. In complete contrast to the $[Fe(CO)_4]^{2-}$ ions in $Na_2Fe(CO)_4 \cdot 1.5(dioxane)$[5] and $K_2Fe(CO)_4$, which show at least one highly distorted (>120°) C–Fe–C angle, the anion in $[Na(crypt)]_2Fe(CO)_4$ is an essentially undistorted tetrahedron (Figure 4). This is no doubt

Table V. Selected Distances and Angles in $[Na(crypt)]_2[Fe(CO)_4]$[a]

Distances (Å) and Angles (deg) in the $[Fe(CO)_4]^{2-}$ Anion			
Fe-C(4)	1.74 (2)	C(4)-O(8)	1.20 (2)
Fe-C(5)	1.81 (2)	C(5)-O(9)	1.13 (2)
Fe-C(6)	1.76 (2)	C(6)-O(10)	1.13 (2)
Fe-C(7)	1.74 (2)	C(7)-O(11)	1.16 (2)
Average	1.762 (17)	Average	1.155 (17)
C(4)-Fe-C(5)	110.6 (9)		
C(4)-Fe-C(6)	108.5 (9)	Fe-C(4)-O(8)	178.6 (18)
C(4)-Fe-C(7)	112.2 (8)	Fe-C(5)-O(9)	176.7 (17)
C(5)-Fe-C(6)	109.5 (8)	Fe-C(6)-O(10)	173.7 (15)
C(5)-Fe-C(7)	108.6 (8)	Fe-C(7)-O(11)	176.8 (14)
C(6)-Fe-C(7)	107.3 (7)	Average	176.7 (10)
Average	109.5 (7)		
Av Distances (Å) and Angles (deg) in the $[Na(crypt)]^+$ Cations			
Na-N	2.802 (36)	C-O-C	115.0 (9)
Na-O	2.532 (16)	O-C-C	112.1 (10)
C-C	1.431 (24)	C-N-C	110.8 (10)
C-N	1.473 (12)	N-C-C	116.3 (18)
C-O	1.432 (13)	C-N-Na	108.1 (5)
		C-O-Na	114.6 (8)
Selected Individual Distances (Å) and Angles (deg) in the $[Na(crypt)]^+$ Cations			
Na(2)-N(12)	2.83 (2)	Na(3)-N(45)	2.88 (2)
Na(2)-O(15)	2.54 (2)	Na(3)-O(48)	2.42 (2)
Na(2)-O(18)	2.48 (2)	Na(3)-O(51)	2.52 (2)
Na(2)-N(21)	2.71 (2)	Na(3)-N(54)	2.79 (2)
Na(2)-O(24)	2.49 (2)	Na(3)-O(57)	2.61 (2)
Na(2)-O(27)	2.55 (2)	Na(3)-O(65)	2.61 (2)
Na(2)-O(32)	2.59 (2)	Na(3)-O(68)	2.46 (2)
Na(2)-O(35)	2.57 (2)	Na(3)-O(60)	2.54 (2)
N(12)-Na(2)-O(15)	66.1 (4)	N(45)-Na(3)-O(60)	64.9 (5)
N(12)-Na(2)-O(27)	65.4 (4)	N(45)-Na(3)-O(65)	65.4 (5)
N(12)-Na(2)-O(32)	65.2 (4)	N(45)-Na(3)-O(48)	65.7 (5)
N(21)-Na(2)-O(18)	68.2 (5)	N(54)-Na(3)-O(51)	64.3 (6)
N(21)-Na(2)-O(24)	67.2 (5)	N(54)-Na(3)-O(57)	64.1 (5)
N(21)-Na(2)-O(35)	65.8 (5)	N(54)-Na(3)-O(68)	66.3 (5)
O(15)-Na(2)-O(18)	64.1 (5)	O(48)-Na(3)-O(51)	67.7 (5)
O(24)-Na(2)-O(27)	64.1 (4)	O(57)-Na(3)-O(60)	66.0 (5)
O(32)-Na(2)-O(35)	63.7 (4)	O(65)-Na(3)-O(68)	66.5 (5)
N(12)-Na(2)-N(21)	177.4 (5)	N(45)-Na(3)-N(54)	176.3 (6)
O(15)-Na(2)-O(24)	162.9 (5)	O(48)-Na(3)-O(68)	162.6 (6)
O(18)-Na(2)-O(32)	171.2 (5)	O(57)-Na(3)-O(65)	173.4 (6)
O(27)-Na(2)-O(35)	163.8 (5)	O(60)-Na(3)-O(51)	161.2 (6)

[a] Standard deviations in parentheses.

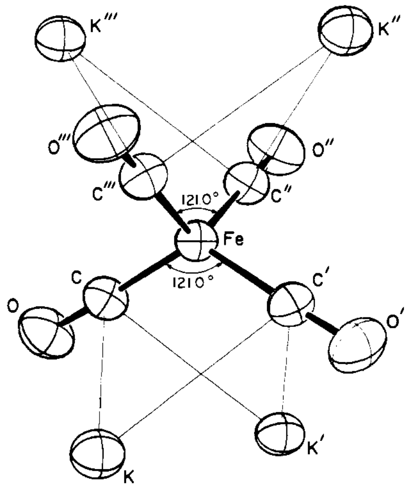


Figure 1. A molecular plot of the $[Fe(CO)_4]^{2-}$ anion in $K_2Fe(CO)_4$ showing the pair of C-Fe-C angles each subtended by a pair of K^+ ions. The K-O, K-C, K-Fe, K-C′, and K-O′ distances are 3.615, 3.280, 3.617, 3.401, and 3.756 Å, respectively, and the C-Fe-C′ angle is 121.0°. Three mutually perpendicular C_2 axes bisect the C-Fe-C angles of the anion.

due to the fact that the cryptate molecule has succeeded in "insulating" the sodium ions, i.e., preventing them from approaching the $[Fe(CO)_4]^{2-}$ ions closely enough to effect geometrical distortions.

The only atoms in close proximity with the sodium cations are the oxygen and nitrogen atoms of the cryptate molecules. Each sodium is completely surrounded by six oxygens and two nitrogens (see Figure 5). Distances and angles are displayed in Table V. These distances are to be compared to the sum of the ionic radius of Na^+ and the van der Waals radius of O and N, giving values of 2.37 and 2.47 Å respectively. The numbering scheme for the molecules is illustrated in Figure 6.

The interactions of crown ethers with alkali metals is very well documented[9] and a great deal of attention has been focused on the "football ligand", cryptate. The ability of this molecule to accommodate alkali metal ions of varying sizes has been studied.[10] As the size of the cation decreases along the series Cs^+, Rb^+, K^+, Na^+, the geometry of the cryptate molecule changes from approximately bicapped trigonal prismatic to approximately bicapped trigonal antiprismatic.[10d] All have D_3 symmetry. This is illustrated by referring to the figure below. The angle α increases from 15 to 45° along the series

Table VI. Dihedral Angles[a] in the Cryptate Molecules

Molecule 1		Molecule 2	
N(12)-C(13)-C(14)-O(15)	−59.7°	55.3°	N(45)-C(46)-C(47)-O(48)
N(12)-C(30)-C(31)-O(32)	−57.8°	56.2°	N(45)-C(63)-C(64)-O(65)
N(12)-C(29)-C(28)-O(27)	−57.8°	63.2°	N(45)-C(62)-C(61)-O(60)
O(18)-C(19)-C(20)-N(21)	−49.0°	(−28°)[b]	O(51)-C(52)-C(53)-N(54)
O(35)-C(36)-C(37)-N(21)	(6°)[b]	(30°)[b]	O(68)-C(69)-C(70)-N(54)
O(24)-C(23)-C(22)-N(21)	47.7°	(5°)[b]	O(57)-C(56)-C(55)-N(54)
O(15)-C(16)-C(17)-O(18)	−59.3°	66.6°	O(48)-C(49)-C(50)-O(51)
O(24)-C(25)-C(26)-O(27)	−63.1°	62.0°	O(57)-C(58)-C(59)-O(60)
O(32)-C(33)-C(34)-O(35)	−68.2°	53.0°	O(65)-C(66)-C(67)-O(68)
C(13)-C(14)-O(15)-C(16)	−89.3°	82.7°	C(46)-C(47)-O(48)-C(49)
C(14)-O(15)-C(16)-C(17)	−179.7°	158.3°	C(47)-O(48)-C(49)-C(50)
C(16)-C(17)-O(18)-C(19)	−178.3°	180.6°	C(49)-C(50)-O(51)-C(52)
C(17)-O(18)-C(19)-C(20)	−77.5°	147.3°	C(50)-O(51)-C(52)-C(53)
C(22)-C(23)-O(24)-C(25)	−163.2°	131.2°	C(55)-C(56)-O(57)-C(58)
C(23)-O(24)-C(25)-C(26)	170.3°	−175.3°	C(56)-O(57)-C(58)-C(59)
C(25)-C(26)-O(27)-C(28)	−167.2°	163.1°	C(58)-C(59)-O(60)-C(61)
C(26)-O(27)-C(28)-C(29)	−74.7°	74.3°	C(59)-O(60)-C(61)-C(62)
C(30)-C(31)-O(32)-C(33)	−83.6°	87.0°	C(63)-C(64)-O(65)-C(66)
C(31)-O(32)-C(33)-C(34)	−168.1°	189.0°	C(64)-O(65)-C(66)-C(67)
C(29)-N(12)-C(13)-C(14)	155.9°	−148.1°	C(63)-N(45)-C(46)-C(47)
C(30)-N(12)-C(13)-C(14)	−85.3°	83.2°	C(62)-N(45)-C(46)-C(47)

[a] Note that the two sets of dihedral angles are roughly mirror images of each other, indicating that the two molecules have opposite chirality.
[b] Dihedral angles associated with disordered ethylene groups.

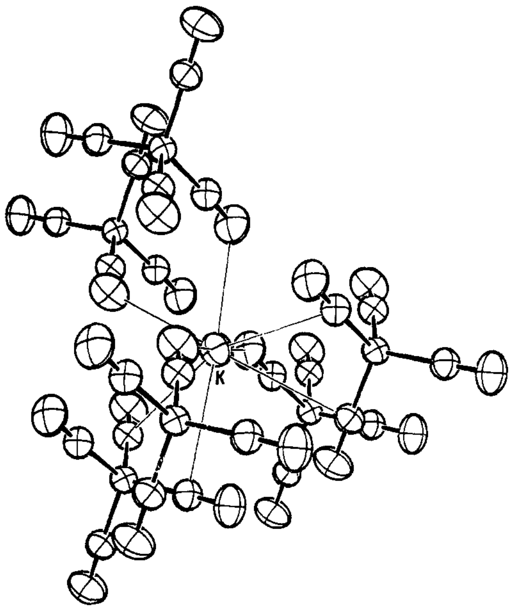
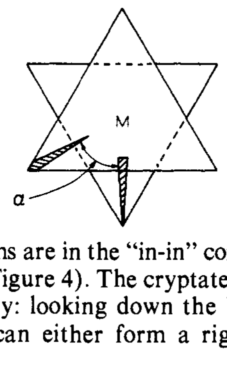


Figure 2. A view of the coordination about K^+, showing coordination from the oxygen atoms of four different $[Fe(CO)_4]^{2-}$ groups and from the C-Fe-C regions of two other $[Fe(CO)_4]^{2-}$ anions.

$Cs^+ \rightarrow Na^+$. In the present compound both cryptates have the value of 45.3° for α.



The nitrogen atoms are in the "in-in" configuration for each cryptate complex (Figure 4). The cryptate molecule possesses an inherent chirality: looking down the N-Na-N axis, the oxygen molecules can either form a right-handed or left-handed screw (see Figure 5). Interestingly, in our structure both right- and left-handed molecules are present (in a strict 1:1 ratio) even though the space group does not have a center of symmetry: in other words, the two independent molecules have opposite chiralities.

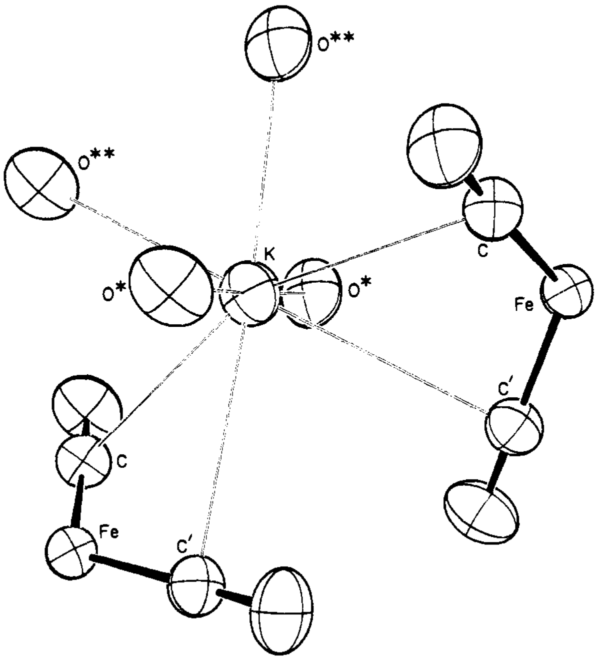


Figure 3. A blow-up of the central region in Figure 2. The exact coordination about K^+ is difficult to define: there are eight atoms within 3.4 Å of K^+, 14 within 3.6 Å, and 20 within 3.8 Å. The shortest contacts are to the four oxygen atoms shown here. Distances indicated in this diagram are K-O* = 2.709, K-O** = 2.876, K-C = 3.280, K-C′ = 3.401, and K-Fe = 3.617 Å. A twofold rotation axis bisects the O**-K-O** angle.

Moras and Weiss have studied the dihedral angles in cryptate-alkali metal complexes in an effort to characterize them.[9e] A listing of these angles for our structure is presented in Table VI. The opposite chiralities of the two molecules are evident upon examination of the values.

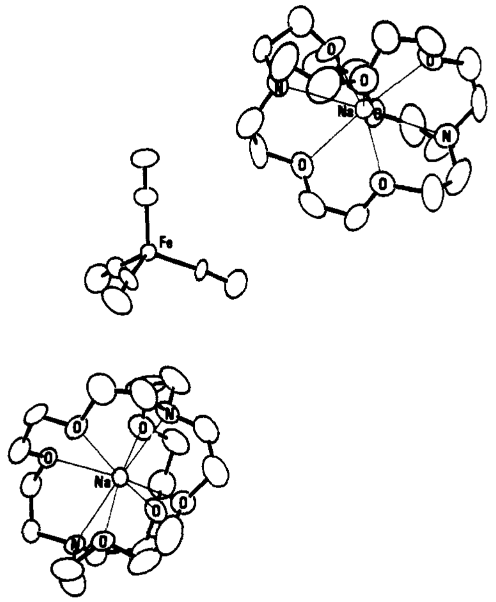


Figure 4. Complete molecular plot of [Na(crypt)]$_2$[Fe(CO)$_4$], showing the two independent [Na(crypt)]$^+$ cations and the [Fe(CO)$_4$]$^{2-}$ anion, which in this case assumes an undistorted tetrahedral geometry.

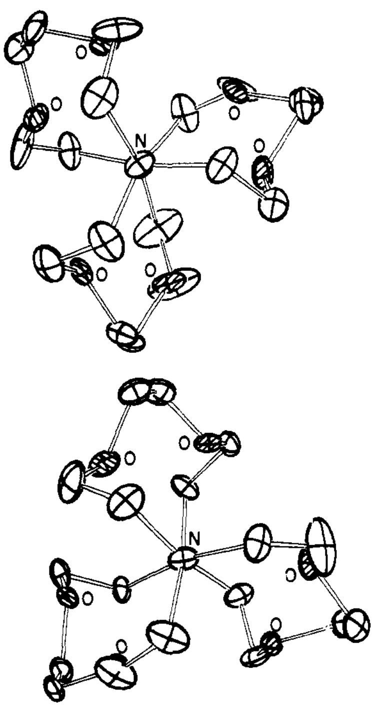


Figure 5. Projections down the N-Na-N axes of the two [Na(crypt)]$^+$ cations, showing the opposite chiralities of the two independent molecules. In both plots the Na atom and the lower N atom are obscured by the upper N atom. Note that the six oxygen atoms define a twisted prismatic arrangement.

Disorder in a few ethylene groups of the [Na(crypt)]$^+$ ions is observed in four portions of the two cryptate molecules [C(36)-C(37), C(52)-C(53), C(55)-C(56), C(69)-C(70)]. Observations that characterize this disorder are: (i) planarity of the X-C-C-X (X = N or O) fragment (i.e., a dihedral angle near zero), and (ii) large anisotropic thermal parameters perpendicular to this plane. Disorder of this kind can contribute to a large R factor as is observed here. It should be also noted that R factors of the order of 10% are not unusual in crystal structures of crown ethers.[9a,10a]

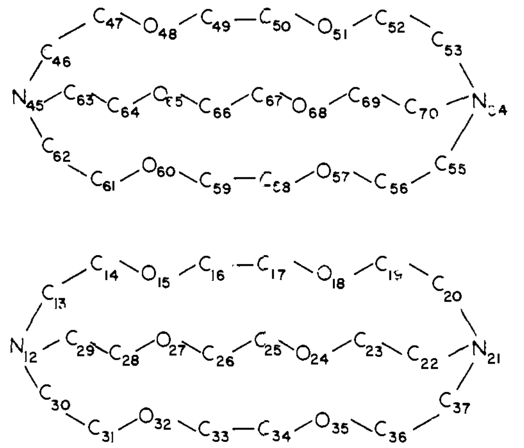


Figure 6. Numbering scheme for the cryptate molecules used in Tables III, V, and VI.

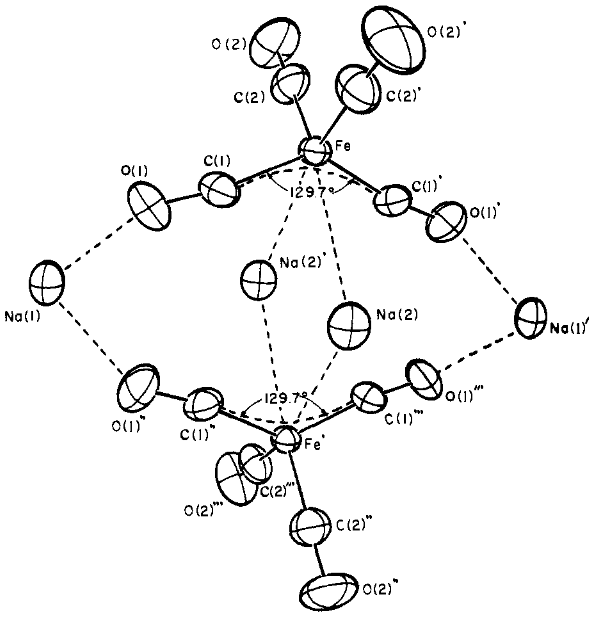


Figure 7. Molecular plot of a portion of the Na$_2$Fe(CO)$_4$·1.5(dioxane) structure which was published earlier (ref 5). Note again the distinctive feature of a distorted C-Fe-C angle subtended by two alkali metal cations (compare this with the plot of K$_2$Fe(CO)$_4$ shown in Figure 1). In the sodium salt the cations are solvated. The magnitude of the distortion in Na$_2$Fe(CO)$_4$·1.5(dioxane) is greater (C-Fe-C = 129.7°) than that in K$_2$Fe(CO)$_4$ (C-Fe-C = 121.0°). Distances of various atoms from Na(2) are: O(1), 3.668; C(1), 3.050; Fe, 3.086; C(1)', 2.860; O(1)', 3.389 Å.

Discussion

As was mentioned in the Introduction, the motivation for investigating the structures of K$_2$Fe(CO)$_4$ and [Na(crypt)]$_2$[Fe(CO)$_4$] came from the dramatic effect of ion pairing upon the solution chemistry of Na$_2$Fe(CO)$_4$ and a desire to see how the geometry of the [Fe(CO)$_4$]$^{2-}$ would be affected by a change of counterion. In the structure of Na$_2$Fe(CO)$_4$·1.5(dioxane),[5] the most notable feature is a large distortion of one of the C-Fe-C angles, presumably caused by the close approach of a sodium ion to the C-Fe-C region of the anion (Figure 7).

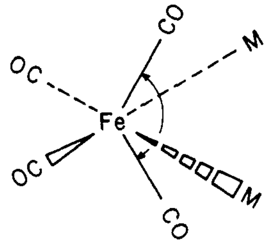
The situation is rather similar in K$_2$Fe(CO)$_4$: again we see a curious association of the alkali metal ions with the C-Fe-C region of [Fe(CO)$_4$]$^{2-}$ (Figure 1). The main differences between the two structures are that in K$_2$Fe(CO)$_4$ the alkali metal ions are not solvated, and two C-Fe-C angles (as opposed to one in the sodium salt) are distorted. The M···C distances in the two structures agree quite well (Table VII) if the

Table VII. Comparison between the $M^+\cdots C$-Fe-C Regions of $Na_2Fe(CO)_4\cdot 1.5$(dioxane) and $K_2Fe(CO)_4$

	$Na_2Fe(CO)_4\cdot$ 1.5 (dioxane) (ref 5)	$K_2Fe(CO)_4$ (this work)	Difference[a]
$M^+\cdots C(1)$, Å	2.86	3.28	0.42
$M^+\cdots Fe$, Å	3.09	3.62	0.53
$M^+\cdots C(1)'$, Å	3.05	3.41	0.36

[a] For comparison, the difference between the covalent radii of Na^+ and K^+ is 0.38 Å.

Table VIII. Correlation between $M\cdots Fe$ Distance and C-Fe-C Angle in a Number of Compounds Containing the $Fe(CO)_4$ Moiety



Compd	M	$M\cdots Fe$ distance, Å	C-Fe-C angle, deg	Ref
$[Na(crypt)]_2[Fe(CO)_4]$	Na	7.18	109.5	This work
$K_2Fe(CO)_4$	K	3.62	121.0	This work
$Na_2Fe(CO)_4\cdot 1.5$(dioxane)	Na	3.09	129.7	5
$[(bipy)CdFe(CO)_4]_3$	Cd	2.64	139.5	12
$[CdFe(CO)_4]_4$	Cd	2.56	154.7	12

difference in covalent radii between Na^+ and K^+ (0.38 Å)[11] is taken into account. The $K\cdots Fe$ distance (3.62 Å), however, is significantly longer than the $Na\cdots Fe$ distance (3.09 Å), suggesting a weaker $M^+\cdots Fe$ interaction in $K_2Fe(CO)_4$. This fact, coupled with the lower charge density of K^+ relative to Na^+, is consistent with the lower degree of angular distortion in $K_2Fe(CO)_4$ (C-Fe-C = 121.0°) as compared with $Na_2Fe(CO)_4\cdot 1.5$(dioxane) (C-Fe-C = 129.7°).

It is instructive to compare these results with the structures of two very interesting compounds, $[(bipy)CdFe(CO)_4]_3$ and $[CdFe(CO)_4]_4$, solved recently by Marks and Ernst.[12] As one proceeds along the series (a) $[Na(crypt)]_2[Fe(CO)_4]$, (b) $K_2Fe(CO)_4$, (c) $Na_2Fe(CO)_4\cdot 1.5$(dioxane), (d) $[(bipy)CdFe(CO)_4]_3$, (e) $[CdFe(CO)_4]_4$, one subjects the $[Fe(CO)_4]^{2-}$ moiety to a range of $M\cdots Fe$ interactions: from zero interaction (a), to weak, largely ionic interactions (b, c), to strong, essentially covalent interactions (d, e). During this transition, one observes a continuing decrease in the $M\cdots Fe$ distance, coupled with an increasing distortion of the C-Fe-C angle (Table VIII). It is as though we had taken a series of "stop action" photographs of the iron atom being attacked by two electrophiles: as the M-Fe distances in the $M\cdots Fe\cdots M$ fragment decrease, the $Fe(CO)_4$ moiety gradually changes from a tetrahedral species to a distorted octahedral fragment.

Our results confirm earlier ideas[2-5] that when highly charged species are brought into close contact with metal carbonylate anions, distortions in the geometry of the latter species are often observed. The degree of distortion is expected to be proportional to the charge density of the cationic species. When the alkali metal ions are "isolated" from the system, as in $[Na(crypt)]_2[Fe(CO)_4]$, the $[Fe(CO)_4]^{2-}$ collapses back into the expected tetrahedral geometry. In addition, when coupled with previous solution studies of the $[Co(CO)_4]^-$ and $[Mn(CO)_5]^-$ systems,[2,3] our results strongly suggest two types of solution cation binding sites within the $[Fe(CO)_4]^{2-}$ moiety. One is a linear interaction with a carbonyl oxygen, $Fe-CO\cdots M^+$, while the other involves a close approach of M^+ to the C-Fe-C region of $[Fe(CO)_4]^{2-}$.

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

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(7) $R = \Sigma \,|F_o - |F_c|\,|/\Sigma F_o$; $R_w = \{\Sigma w|F_o - |F_c|\,|^2/\Sigma wF_o^2\}^{1/2}$.

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