

Acta Cryst. (1975). B31, 2927

Sodium formate

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(Received 27 June 1975; accepted 21 July 1975)

Abstract. CHNaO₂, monoclinic, *C*2/*c* (*C*_{2n}^h), *a* = 6.259 (1), *b* = 6.757 (2), *c* = 6.172 (1) Å, β = 116.14 (1)°, *Z* = 4, *D*_x = 1.928 g cm⁻³, μ(Cu *K*α) = 30.85 cm⁻¹. The formate ion has *C*_{2v} symmetry, C–O = 1.246 (1) Å, C–H = 0.99 (2) Å, O–C–O = 126.3 (2), O–C–H = 116.9 (1)°. The Na ion has six O neighbours at 2.40–2.52 Å.

Introduction. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer, with Cu *K*α radiation, θ–2θ scan, and check-reflexion scaling. Two data sets were collected, and the averaged set contained 253 independent reflexions, of which two had *I* < 3σ(*I*) [*σ*²(*I*) = *S* + *B* + (*dS*)², *S* = scan, *B* = background count; *d* was taken as 0.05 on the basis of previous experience]. The crystal had dimensions 0.3 × 0.3 × 0.3 mm and no absorption correction was applied. Intensity statistics were inconclusive, and the structure was solved by direct methods applied in both *Cc* and *C*2/*c*; only the centrosymmetric space group gave a satisfactory solution, and refinement proceeded in *C*2/*c*. All atoms, including H, were refined, and partial atomic charges were estimated by separating the core and valence electrons and refining occupancy parameters for the valence electrons (Corfield & Shore, 1973). The total net charge on the anion was –0.79 e, and the Na scattering factor was modified to correspond to a charge of +0.79. The final *R* for all 253 reflexions* was 0.022 (three reflexions, 110, 020, and 002, were given zero weight in the final cycles because of suspected extinction errors); the function minimized

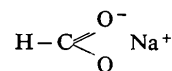
* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31294 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

was $\sum w(F_o - F_c)^2$, and final $w = (0.0313 + 0.0137|F_o| - 0.0027|F_o|^2 + 0.0001|F_o|^3)^{-1}$ gave constant average values of $w(F_o - F_c)^2$ as a function of $|F_o|$. Final positional and thermal parameters are in Table 1.

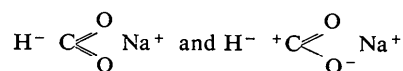
Discussion. The structure is as previously determined (Zachariasen, 1940) [except that the previous study used an orientation *C*2/*n*; the previous cell can be transformed to the present conventional cell by the matrix (100/010/101)]. The present study was undertaken to determine more accurate atomic positions, particularly for the H atom, to assist an e.s.r. and ENDOR study.

The formate anion lies on a twofold axis and has *C*_{2v} symmetry, C–O = 1.246 (1), C–H = 0.99 (2) Å, O–C–O = 126.3 (2), O–C–H = 116.9 (1)°. These dimensions are similar to those in other formates. The Na ion has six O neighbours from five different formate ions, Na–O = 2.401, 2.434, and 2.519 (1) Å (each × 2).

The electron distribution (Table 1) indicates a charge of –0.23 e on each O, –0.49 e on H, +0.79 e on Na, and a small charge of +0.16 e on C. This suggests that in addition to resonance structures of the type



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also contribute to the overall structure. The Na...H distance along the twofold axis is 2.94 (2) Å, and a final difference map exhibits some build-up of density between these atoms, which suggests some interaction. These structural features are in accord with the physical

Table 1. *Positional and thermal parameters (standard deviations in parentheses)*

		T.F. = exp [–2π ² (10 ⁻²) (h ² a* ² U ₁₁ + ... + 2hka*b*U ₁₂ + ...)]						
		Zachariasen (1940)			Present analysis			
	<i>z</i> – <i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	Charge	
Na	0	–0.139	$\frac{1}{4}$	0	–0.1380 (1)	$\frac{1}{4}$	+0.79 (14)	
O	0.142	0.194	0.185	0.1357 (2)	0.1966 (2)	0.1796 (2)	–0.23 (1)	
C	0	0.283	$\frac{1}{4}$	0	0.2799 (2)	$\frac{1}{4}$	+0.16 (3)	
H	0	0.43	$\frac{1}{4}$	0	0.4268 (30)	$\frac{1}{4}$	–0.49 (10)	
		<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	
Na		1.74 (3)	2.38 (4)	1.79 (3)	0	0.76 (2)	0	
O		1.84 (5)	3.16 (6)	2.18 (5)	0.21	1.01 (4)	0.41 (3)	
C		2.67 (7)	2.08 (7)	2.13 (7)	0	0.90 (5)	0	
H		Isotropic <i>U</i> = 6.1 (8) × 10 ⁻² Å ²						

properties; sodium formate is reported to decompose on gentle heating to sodium oxalate and hydrogen (Vogel, 1959), which indicates that the C-H bond is easily broken.

We thank the National Research Council of Canada for financial support, and the University of British Columbia Computing Centre for assistance.

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Acta Cryst. (1975). **B31**, 2928

Tetraphenylferrole-Fe(CO)₃: a Cycloheptatrieneiron Tricarbonyl-Diphenylacetylene Reaction Product

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(Received 23 June 1975; accepted 21 July 1975)

Abstract. [(C₆H₅)₄C₄]Fe₂(CO)₆, monoclinic, $P2_1$, $a = 16.464$ (2), $b = 7.822$ (2), $c = 11.374$ (2) Å, $\beta = 98.14$ (1)° at *ca.* -40°C, D_c (-40°C) = 1.463, D_m (22°C) = 1.448 g cm⁻³, $Z = 2$. The molecule consists of two Fe(CO)₃ moieties joined by a normal Fe-Fe single bond [2.505 (1) Å], with one Fe σ -bonded to the terminal carbons of a tetraphenyl-substituted butadiene group - thereby forming a ferracyclopentadiene ring - and with the other Fe coordinated with the π electrons of the butadiene residue. Full-matrix least-squares refinement has converged with a weighted R index (on $|F|$) of 0.051 using the 2465 reflections with $I_o > 2.0\sigma(I_o)$.

Introduction. Single crystals of [(C₆H₅)₄C₄]Fe₂(CO)₆ formed as thin yellow-orange plates from an argon-

degassed ether/methanol solution at *ca.* 5°C. Preliminary X-ray diffraction experiments conducted with a Syntex $P2_1$ automated four-circle diffractometer indicated the symmetry and systematic reflection absences consistent with monoclinic space groups $P2_1$ or $P2_1/m$. Intensity data collection details are given in Table 1. Standard deviations were assigned to the data and the usual corrections applied, including that for absorption (see Table 1), as described elsewhere (Riley & Davis, 1976). Only the 2465 reflections with $I > 2.0\sigma(I)$ were used in the ensuing solution and refinement of the structure.

Solution of the Patterson map suggested the non-centrosymmetric space group $P2_1$, and indicated the presence of two Fe atoms per asymmetric unit, separated by *ca.* 2.5 Å. Three successive difference maps, phased initially with the two Fe atoms, revealed the positions of all remaining non-hydrogen atoms of the structure. Full-matrix least-squares refinement, with the phenyl rings treated as rigid groups of D_{6h} symmetry (C-C = 1.392 Å, C-H = 1.00 Å, C-C-C = 120°), and non-group atoms ultimately as anisotropic thermal ellipsoids, converged with $R = \sum[|F_o| - |F_c|] / \sum|F_o| = 0.062$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.052$. The function minimized in refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights w are $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation $|F_o|$. Neutral atom scattering factors for Fe, O, C (Cromer & Waber, 1965) and H (Stewart, Davidson & Simpson, 1965) were used. Corrections for the real ($\Delta f'$) and imaginary ($\Delta f''$) parts of anomalous scattering of Mo $K\alpha$ radiation were applied to the Fe scattering function (Cromer, 1965).

To determine whether the correct enantiomorph had been selected, additional cycles of least-squares refinement were carried out to convergence with the mirror

Table 1. *Experimental summary for*
[(C₆H₅)₄C₄]Fe₂(CO)₆

Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT-1 low-temperature flow system
 Radiation: Mo $K\alpha$, $\lambda = 0.71069$ Å
 Mode: ω scan technique, recentered automatically after each batch of 750 reflections
 Scan range: symmetrically over 1.0° about the $K\alpha_{1,2}$ maximum
 Scan rate: variable, 1.5° to 4.0° min⁻¹
 Background: offset 1.0° and -1.0° in ω from $K\alpha_{1,2}$ maximum
 Check reflections: four remeasured after every 96 reflections; analysis* of 37 sets of check reflections indicated random fluctuation not exceeding 1.3% or 0.1 of an e.s.d. of the initial intensity set
 3145 reflections measured in octants h,k,l and \bar{h},k,l ; $4^\circ \leq 2\theta \leq 52.5^\circ$
 Data crystal faces: six faces of {100}, {010}, {001}
 Data crystal dimensions: 0.05 × 0.70 × 0.20 mm parallel to directions **a, b, c**
 Data crystal volume = 0.00764 mm³
 Absorption coefficient: $\mu(\text{Mo } K\alpha) = 10.7$ cm⁻¹
 Transmission factor range: 0.81 to 0.95

* Henslee & Davis (1975).