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The Crystal Structure of a Compound, Dibenzosemibullvaleneiron Tetracarbonyl, Containing a New Four-Membered Ring System (Ferretane)

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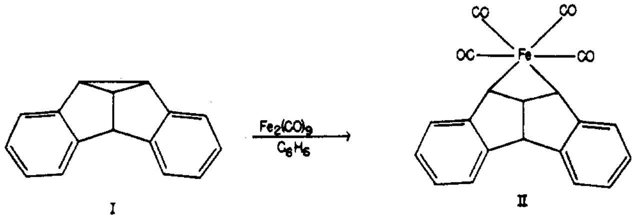
Received August 27, 1973

AIC306356

The reaction of dibenzosemibullvalene with diiron nonacarbonyl produces a molecule which contains a new four-membered ring system, ferretane, in which the Fe is σ bonded to two carbon atoms. The stereoconfiguration of this product was established by X-ray single-crystal analysis. The molecule crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.365$ (4) Å, $b = 18.355$ (8) Å, $c = 9.816$ (4) Å, and $\beta = 106.0$ (1)°, and its structure was solved by the symbolic addition procedure. The 2849 independent X-ray intensities were collected on an automatic diffractometer (Mo Kα radiation) and refined by full-matrix least-squares methods to a final R factor of 4.4%. The ferretane ring is planar with Fe–C σ bond lengths of 2.141 (3) and 2.137 (3) Å.

Introduction

It has been reported that diiron nonacarbonyl enters into rearrangement reactions with several polycyclic olefins which contain cyclopropane rings.[1-2] The bonding between the $Fe(CO)_3$ fragment and the modified unsaturated hydrocarbons usually involves σ and π allyl type bonds. This has been noted for the reaction of $Fe_2(CO)_9$ with bullvalene,[3] azabullvalene,[4] and semibullvalene.[5] However, the reaction of $Fe_2(CO)_9$ with dibenzosemibullvalene (I)[6-7] follows a significantly different pathway. In this case the iron atom is inserted into a σ bond of the three-membered ring to yield a new type of four-membered ring containing iron bonded by two Fe–C σ bonds (II); a ferretane ring. Molecules containing two Fe–C σ bonds have been encountered previously[8-10] but this is the first time it occurs in a four-membered ring. A note on the chemistry of the molecule and a preliminary report of the structure have been published.[11]



I

II

Experimental Section

The crystals used in the X-ray analysis were kindly provided by Professor R. M. Moriarty of the University of Illinois. Information on data collection and physical quantities for the crystal are listed in Table I. Lorentz and polarization corrections were applied and normalized structure factor magnitudes $|E|$ as well as structure factor magnitudes $|F|$ were derived.

The structure was solved by routine application of the symbolic addition procedure for centrosymmetric crystals[12] using computer programs written by R. D. Gilardi and S. A. Brenner of this laboratory.

Table I

Molecular formula	$FeC_{20}H_{12}O_4$
Molecular wt	371.162
Crystal size	~(0.4 × 0.8 × 0.7 mm)
Space group	$P2_1/n$
a	9.365 (4) Å
b	18.355 (8) Å
c	9.816 (4) Å
β	106.0 (1)°
Z	4
Density (calcd)	1.52 g/cm³
μ	9.64 cm⁻¹
Radiation	Mo Kα (0.71069 Å) Zr filter
Data collection	Automatic computer controlled four circle diffractometer at room temperature
Collection technique	θ–2θ scan
Scan width	$1.3° + 2\theta(\alpha_2) - 2\theta(\alpha_1)$
Scanning speed	2°/min
Background time	10 sec
Maximum sin θ/λ	0.703
No. of independent reflections	2965

Coordinates and thermal factors were refined on F values using a full-matrix least-squares procedure.[13] Scattering factors used were those listed in Vol III of the International Tables for X-ray Crystallography. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weighting function w was calculated according to eq 1.

$$w^{-1} = \sigma_F^2 = \left[\frac{Q(P - t_f(B_1 + B_2))}{4LP}\right] \times \left[\frac{P + C^2P^2 + t_f^2(B_1 + B_2 + C^2B_1^2 + C^2B_2^2)}{(P - t_f(B_1 + B_2))^2} + \frac{\sigma_Q^2}{Q}\right] \quad (1)$$

Q = attenuator factor, P = peak count, B_1B_2 = background counts, t_f = time factor to put background and peaks on same scale, and c = instrumental reliability factor (0.02). A detailed derivation of this weighting function is given by Gilardi.[14] In addition, to conserve computing time, all reflections for which $|F_o| < 3.0(\sigma_{|F_o|})$ were given zero weight and excluded from the refinement. No absorption corrections were applied. All 12 hydrogen atoms were located in a difference map and their positions were included in the least squares as constants. The hydrogen atoms were assigned thermal parameters equal to those of the atoms to which they were bonded. The final R factor, where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, was 0.044 for data used

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(13) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(14) R. D. Gilardi, *Acta Crystallogr., Sect. B*, 29, 2089 (1973).

Table II. Fractional Coordinates and Thermal Parameters[a] with Standard Deviations[b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
FE	0.8495 (0)	0.3506 (0)	0.3611 (0)	3.62 (2)	3.27 (2)	3.21 (2)	−0.34 (2)	0.94 (1)	−0.18 (2)
C(1)	0.6933 (3)	0.3832 (2)	0.5457 (3)	5.21 (16)	3.03 (13)	2.85 (13)	−0.11 (11)	1.09 (12)	−0.23 (10)
C(2)	0.7564 (3)	0.3092 (2)	0.5218 (3)	4.19 (15)	3.55 (13)	3.10 (13)	−0.08 (11)	0.99 (11)	−0.06 (11)
C(3)	0.6306 (3)	0.2589 (2)	0.4788 (3)	5.08 (16)	2.88 (13)	3.02 (12)	0.14 (12)	1.53 (12)	0.19 (10)
C(4)	0.6314 (4)	0.1845 (2)	0.4541 (3)	5.87 (19)	3.03 (13)	4.83 (15)	0.20 (13)	2.12 (14)	0.27 (11)
C(5)	0.4968 (4)	0.1469 (2)	0.4186 (4)	7.21 (21)	3.13 (15)	5.25 (16)	−0.58 (16)	2.60 (15)	0.04 (14)
C(6)	0.3648 (4)	0.1827 (2)	0.4084 (4)	6.29 (20)	4.09 (16)	5.08 (17)	−1.25 (15)	2.29 (15)	−0.26 (13)
C(7)	0.3641 (4)	0.2566 (2)	0.4323 (4)	4.92 (18)	4.24 (16)	4.78 (16)	−0.43 (14)	2.00 (14)	0.09 (13)
C(8)	0.4964 (4)	0.2945 (2)	0.4670 (3)	5.07 (16)	3.23 (13)	2.83 (13)	0.06 (12)	1.63 (12)	0.13 (10)
C(9)	0.5210 (4)	0.3749 (2)	0.4985 (3)	5.12 (16)	3.17 (12)	3.53 (14)	0.37 (11)	1.94 (12)	−0.06 (10)
C(10)	0.4718 (4)	0.4237 (2)	0.3710 (3)	4.99 (16)	2.67 (13)	3.89 (14)	0.75 (11)	1.81 (13)	−0.59 (11)
C(11)	0.3295 (4)	0.4362 (2)	0.2872 (4)	4.93 (18)	4.10 (16)	5.45 (17)	1.01 (14)	2.03 (15)	−0.13 (14)
C(12)	0.3058 (4)	0.4831 (2)	0.1733 (4)	5.71 (21)	4.56 (16)	4.90 (18)	1.53 (15)	1.35 (16)	−0.10 (14)
C(13)	0.4250 (4)	0.5181 (2)	0.1437 (3)	6.90 (20)	3.66 (15)	3.88 (15)	1.54 (14)	1.76 (15)	0.15 (12)
C(14)	0.5685 (4)	0.5053 (2)	0.2258 (3)	6.01 (20)	3.30 (14)	3.91 (14)	0.41 (13)	1.86 (14)	−0.11 (11)
C(15)	0.5925 (3)	0.4573 (2)	0.3396 (3)	5.29 (16)	2.57 (12)	3.36 (13)	0.25 (11)	1.55 (12)	−0.55 (11)
C(16)	0.7339 (4)	0.4341 (2)	0.4391 (3)	5.15 (16)	2.83 (13)	3.59 (13)	−0.32 (12)	1.31 (12)	−0.39 (11)
C(17)	0.9036 (4)	0.4137 (2)	0.2432 (4)	4.42 (17)	4.39 (16)	5.10 (18)	−0.41 (13)	1.51 (14)	−0.05 (14)
O(18)	0.9318 (3)	0.4577 (2)	0.1738 (3)	7.47 (16)	5.68 (14)	7.13 (16)	−0.60 (12)	3.69 (13)	1.38 (13)
C(19)	1.0040 (4)	0.3735 (2)	0.5100 (4)	5.22 (18)	4.68 (17)	5.37 (18)	−0.99 (14)	1.77 (16)	0.03 (14)
O(20)	1.1007 (3)	0.3874 (2)	0.6038 (3)	5.79 (14)	9.40 (18)	5.88 (15)	−2.71 (13)	−0.72 (12)	−0.66 (13)
C(21)	0.9304 (4)	0.2649 (2)	0.3283 (4)	4.96 (18)	5.00 (19)	4.01 (16)	0.08 (15)	1.17 (14)	0.20 (14)
O(22)	0.9769 (3)	0.2095 (1)	0.3094 (3)	7.96 (16)	5.73 (14)	6.64 (16)	2.48 (12)	2.06 (13)	−0.59 (12)
C(23)	0.6768 (4)	0.3272 (2)	0.2304 (3)	4.95 (17)	3.32 (14)	3.69 (15)	−0.12 (12)	1.88 (14)	−0.32 (11)
O(24)	0.5735 (3)	0.3111 (1)	0.1457 (2)	4.75 (12)	6.12 (13)	4.22 (12)	−0.82 (10)	0.56 (10)	−1.30 (10)
H(1)	0.734	0.398	0.654						
H(2)	0.841	0.294	0.602						
H(4)	0.730	0.156	0.471						
H(5)	0.515	0.091	0.420						
H(6)	0.274	0.146	0.389						
H(7)	0.264	0.279	0.413						
H(9)	0.464	0.392	0.580						
H(11)	0.235	0.412	0.304						
H(12)	0.202	0.494	0.098						
H(13)	0.417	0.553	0.055						
H(14)	0.654	0.534	0.219						
H(16)	0.808	0.481	0.473						

[a] The thermal parameters are of the form $T = \exp[{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
[b] Standard deviations are based solely on least-squares parameters.

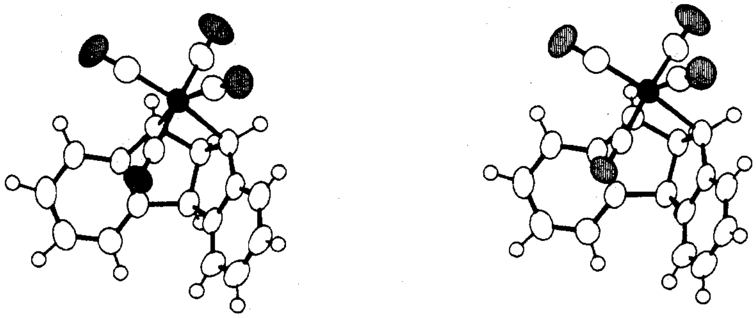


Figure 1. Stereoconfiguration of dibenzosemibullvaleneiron tetracarbonyl, showing thermal vibration ellipsoids corresponding to the final thermal parameters. The isotropic hydrogen atoms are shown at their refined positions. The Fe atom is indicated by ● and the oxygen atoms are indicated by ◍.

in the refinement (2387 reflections). For the full set of data (2965 reflections) the final R factor was 0.062. The final weighted R factors, where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, were 0.039 for the data used in the refinement and 0.042 for the full set of data. At the end of the refinement procedure the standard deviation of an observation of unit weight ($[\Sigma w(|F_o| - |F_c|)^2/(M - N)]^{1/2}$ where $M = 2387$ and $N = 226$) was 1.34. The average parameter shift during the final cycle of least-squares refinement was 0.0051 Å. The largest shift was 0.0197 Å. Coordinates and thermal parameters for the molecule are listed in Table II.

Discussion

The stereoconfiguration of the molecule is illustrated in Figure 1. The dibenzosemibullvalene portion of the molecule is composed of two planar segments; atoms C(1) to C(9), planar to within ±0.075 Å and atoms C(9) to C(16) plus C(1), planar to within ±0.033 Å. The angle between the two planes is 61.5°. The ferretane ring is planar to

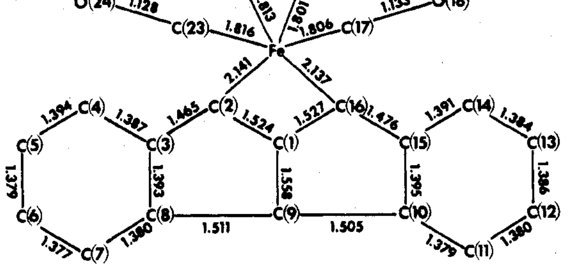
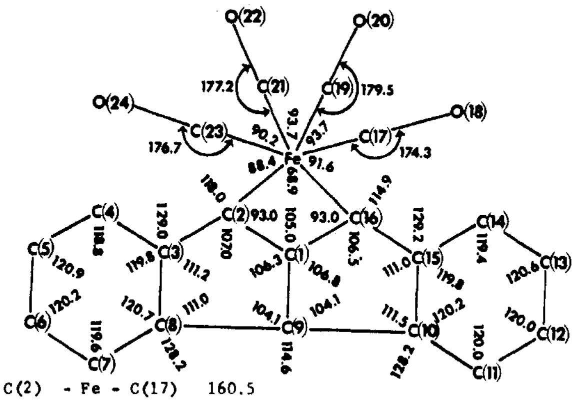


Figure 2. Bond distances: based solely on least-squares parameters standard devisions are ±0.003 Å for Fe–C bonds, ±0.004 for C=O bonds and ±0.005 Å for C–C bonds.



C(2) - Fe - C(17)	160.5		
C(2) - Fe - C(19)	83.4	C(16) - Fe - C(23)	89.0
C(2) - Fe - C(21)	95.7	C(17) - Fe - C(21)	103.8
C(16) - Fe - C(19)	85.1	C(17) - Fe - C(23)	92.9
C(16) - Fe - C(21)	164.6	C(19) - Fe - C(23)	171.2

Figure 3. Bond angles: standard deviations are ±0.2° for angles around the Fe atom and ±0.3° for angles around the carbon atoms.

Table III. Deviations (Å) from Least-Squares Planes[a]

Plane A		Plane B		Plane C	
	Δ		Δ		Δ
C(1)	0.075	C(1)	0.017	Fe	0.007
C(2)	−0.013	C(16)	−0.033	C(2)	−0.010
C(3)	−0.030	C(15)	−0.001	C(1)	0.013
C(4)	−0.013	C(14)	0.014	C(16)	−0.010
C(5)	0.015	C(13)	0.013		
C(6)	0.028	C(12)	−0.013		
C(7)	0.006	C(11)	−0.011		
C(8)	−0.026	C(10)	0.007		
C(9)	−0.043	C(9)	0.007		

Plane A: $-1.7802x - 3.4321y + 9.6083z = 2.6189$
Plane B: $-2.3392x + 14.4038y + 6.2796z = 7.1671$
Plane C: $6.3935x + 4.2569y + 4.6908z = 8.6100$

[a] The equations are referred to the monoclinic axes and fractional coordinates; the distance is origin to plane distance. All atoms were given equal weights. The planes were calculated according to the method of Schomaker, Waser, Marsh, and Bergman, *Acta Crystallogr.*, 12, 600 (1959).

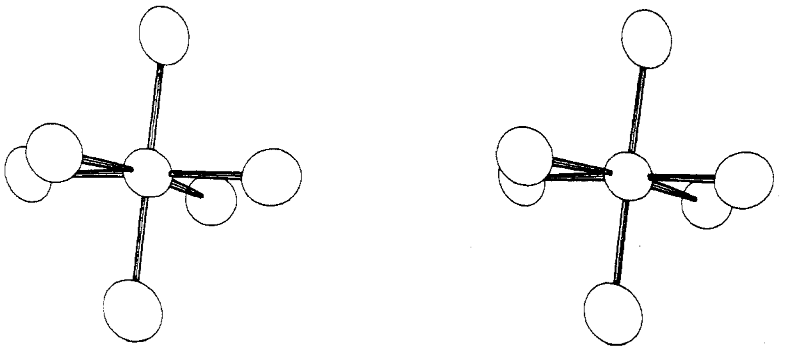


Figure 4. Coordination about the Fe atom. Atoms are shown at their final refined positions with arbitrary isotropic thermal parameters.

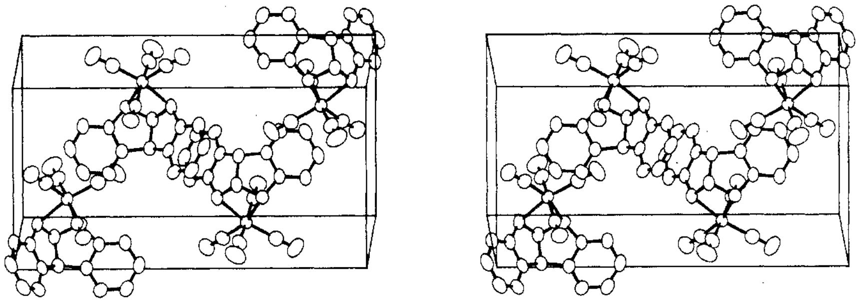


Figure 5. Packing of molecules in one unit cell. It is viewed looking down the *C* axis with *b* → and *a* ↑.

within ±0.013 Å. Standard deviations of individual atoms from these planes are listed in Table III. The bond lengths are illustrated in Figure 2, and the bond angles are shown in Figure 3. The average Fe-C σ bond length is 2.139 (2) Å which is in agreement with distances of 2.09-2.15 Å found in other molecules with similar Fe-C σ bonds.[15,16] Other significant distances in the four-membered ring are Fe· · ·C(1) at 2.691 (3) Å and C(2)· · ·C(16) at 2.421 (4) Å. The Fe-C(0) distances range from 1.801 (4) to 1.816 (4) Å (av = 1.809 (4) Å) with no significant differences between axial and equatorial bonds. The distances and angles in the aromatic rings are well within expected values for such groupings. The average C-C distance is 1.385 (5) Å (maximum deviation is 2σ) and the average C-C-C angle is 120.0 (3)° (maximum deviation is 4σ). All the carbon-carbon single bonds in the five-membered rings, except C(1)-C(9), are shortened due to the conjugative effects of the aromatic rings. However, in the C(8)-C(9) and C(10)-C(9) bonds this effect is partially offset by the repulsive forces between the aromatic rings, particularly between C(8) and C(10). This is further evidenced by the C(8)-C(9)-C(10) angle of 114.6 (3) which is significantly larger than any of the internal angles in the five-membered rings (av = 107.9 (3)°).

The coordination about the Fe atom is octahedral as can be seen in Figure 4. In other Fe tetracarbonyls in which the Fe is also bonded to two other atoms, as part of a three-membered ring, the coordination about the Fe atom is trigonal bypyramid.[16,17] In the three-membered rings in the above molecules, the internal Fe ring angles are on the order

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(15) A. R. Luxmore and M. R. Truter, *Acta Crystallogr.*, 15, 1117 (1970).

(16) C. Kruger, *J. Organometal. Chem.*, 22, 697 (1970).

(17) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1286 (1962).

of 38.1[17] and 48.1°[18] which constrain the Fe atom into the trigonal bypyramid coordination. In the ferretane ring the internal Fe ring angle is 68.9 (2)° which allows the Fe to assume an octahedral coordination.

The packing of the molecules in a unit cell is illustrated in Figure 5. All the stereo illustrations were drawn by a computer using program ORTEP by Johnson.[18] The molecules are held together solely by van der Waals forces. There are no intermolecular contacts less than van der Waals radii. The closest intermolecular approach is O(22)· · ·O(24) at 3.20 Å. The closest C–O approach is C(21)· · ·O(24) at 3.33 Å, the closest C–C approach is C(13)· · ·C(13) at 3.54 Å, and the closest intermolecular approach to the Fe atom is Fe· · ·O(24) at 4.21 Å.

Registry No. Dibenzosimibullvaleneiron tetracarbonyl, 50790-65-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1054.

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Contribution from the Sterling Chemistry Laboratory,
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Crystal Structure, Crystal Forces, and Charge Distribution in Salts of the Tetrachlorozincate Anion

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Received October 2, 1973 AIC30718M

The crystal and molecular parameters of cesium tetrachlorozincate, Cs_2ZnCl_4, have been determined using an X-ray diffraction intensity data set. The crystal system is orthorhombic, space group *Pnam*, with four formula weights per unit cell; the unit cell parameters are $a = 9.7577$ (15), $b = 12.9704$ (16), and $c = 7.4004$ (10) Å. A total of 2119 independent reflections was used in least-squares refinement of the molecular parameters, the R factor (on F) converging to 5.7%. The anion has crystallographically imposed m symmetry and the three independent zinc–chlorine bond lengths are 2.249 (3), 2.259 (3), and 2.252 (2) Å. Analysis of the relationship between crystal force field and the observed anion bond lengths was not successful, presumably because the differences between the lengths of these bonds are so small. After correction for thermal motion, the zinc–chlorine bond length in an isolated anion was estimated to be in the range 2.28–2.31 Å. The structural parameters of hexaamminecobalt tetrachlorozincate chloride, $[Co(NH_3)_6][ZnCl_4][Cl]$, have been reported (D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 9, 465 (1970)) and the tetrachlorozincate anion is significantly distorted in the crystal lattice. The major cause of the bond length distortions is anisotropy in the applied electrostatic crystal forces and the analysis indicated that the charge distribution within the anion is $[Zn^{1.0+}(Cl^{-0.75})_4]^{2-}$, with a bond length in an isolated anion of 2.30 Å (after correction for thermal motion) and a stretching force constant for the zinc–chlorine bond in the anion of 1.31 mdyn/Å. This value for the stretching force constant is 14% larger than that derived by normal-coordinate analysis of the vibrational spectrum, due to a breakdown of the assumption of a linear variation of bond length with applied force. Charge distributions within complex chloro anions can also be obtained from nuclear quadrupole resonance spectra and molecular orbital calculations; comparisons among the results obtained by the three methods, where applicable, for the tetrachlorozincate, tetrachlorocuprate, pentachlorozincate, and pentachlorocuprate anions show an overall agreement in the trends, if not in the absolute magnitudes.

Introduction

The crystal and molecular structure of hexaamminecobalt tetrachlorozincate chloride, $[Co(NH_3)_6][ZnCl_4][Cl]$, has been reported[1] and the tetrachlorozincate anion is markedly distorted from its free equilibrium geometry, which is ideally tetrahedral. It has been shown that distortions of bond lengths within complex anions observed in the solid state can be rationalized in terms of applied crystal forces[2,3] and this approach was applied to the abovementioned distortions, which are the largest known in any structure determined to a high degree of precision.

Cesium tetrachlorozincate has been shown to be isostructural with β-K_2SO_4,[4] but the atomic parameters have not been reported. The structural parameters were determined using X-ray diffraction data collected using a four-circle diffractometer. It was hoped that the complex anion in this salt would be less distorted and that the crystal force analyses in the two $ZnCl_4^{2-}$ salts could be usefully compared; unfortunately the bond lengths in the complex anion in Cs_2ZnCl_4 were so close in magnitude to each other that the crystal force analysis was not successful. However the length of the Zn–Cl bond expected in the absence of crystal forces was similar in the two compounds, providing some support for the validity of the method of crystal force analysis.

The charge distribution within the $ZnCl_4^{2-}$ anion can be derived from the crystal force analysis and also from nuclear quadrupole resonance spectra and molecular orbital calculations. Charge distributions obtained in these ways are compared for this and other complex chloro anions.

Collection and Reduction of X-Ray Diffraction Data for Cs_2ZnCl_4

Crystal Data. Cesium tetrachlorozincate, Cs_2ZnCl_4, mol wt 473.0, is orthorhombic with $a = 9.7577$ (15), $b = 12.9704$ (16),

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[1] D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 9, 465 (1970).

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