possible even at −175 °C. Confer Table XII, which gives the root-mean-square amplitudes of vibration of all atoms at both temperatures.

(39) This value is the average perpendicular distance between N(2) and the toluene plane and C(13) and C(14) and the N(2) pyrrole plane.

(40) All distances are those observed at −175 °C.

(41) The 3.52-Å separation between the organic portions is at the upper limit of values observed for $\pi$ complexes; the 3.30-Å separation between the toluene molecule and the porphyrin core is a typical separation: F. H. Herbstein, "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N.Y., 1971, Chapter 3.

(42) The larger spacing at the toluene methyl portion of the ring may well result from steric interactions between the methyl group and atoms of the porphyrin. See Figure 4. Spacings (3.5 Å) are observed for hexamethylbenzene complexes.[41]

(43) A. Treibs, *Justus Liebigs Ann. Chem.*, **476**, 1 (1929).

(44) H. A. O. Hill, A. J. MacFarlane, and R. J. P. Williams, *J. Chem. Soc. A*, 1704 (1969).

(45) H. A. O. Hill, P. J. Sadler, R. J. P. Williams, and C. D. Barry, *Ann. N.Y. Acad. Sci.*, **206**, 247 (1973).

(46) F. A. Walker, *J. Magn. Reson.*, **15**, 201 (1974).

(47) G. P. Fulton and G. N. LaMar, *J. Am. Chem. Soc.*, **98**, 2119 (1976); G. P. Fulton and G. N. LaMar, *ibid.*, 2124 (1976).

# Molecular Stereochemistry of Phthalocyanatozinc(II)

**W. Robert Scheidt* and W. Dow**

*Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.* *Received July 16, 1976*

**Abstract:** The molecular stereochemistry of phthalocyanatozinc(II) (ZnPc) has been determined by x-ray diffraction methods. The phthalocyanato ligand constrains the zinc atom to effectively square-planar coordination. Surprisingly, the zinc atom has contracted sufficiently to fit into the central hole of the phthalocyanato ligand; the zinc atom is centered or very nearly centered in the plane of the four phthalocyanato nitrogen atoms. The core of the phthalocyanato ligand is somewhat expanded with the average Zn–N bond distance = 1.980 (2) Å. A comparison of the stereochemical parameters of the expanded core of ZnPc with those of the relatively contracted core of FePc shows that the alterations accompanying expansion of the phthalocyanato core are similar to those noted previously for porphyrin derivatives. Crystal data: space group, $P2_1/a$; $a$ = 19.274 (5), $b$ = 4.8538 (15), $c$ = 14.553 (4) Å, $\beta$ = 120.48 (2)°; $\rho_{\text{exptl}}$ = 1.62 and $\rho_{\text{calcd}}$ = 1.614 g/cm$^3$ for $Z$ = 2; required molecular symmetry, $\bar{1}$. Intensity data were measured by $\theta$–$2\theta$ scanning on a Syntex P$\bar{1}$ automated diffractometer using graphite-monochromated Mo K$\alpha$ radiation. The intensities of 4515 unique observed data with $(\sin\theta)/\lambda \leq 0.935$ Å$^{-1}$ were used in the refinement of the 187 structural parameters. Final discrepancy indices: $R_1$ = 0.060; $R_2$ = 0.073.

The genesis of our interest in the molecular structure of four-coordinate phthalocyanatozinc(II), ZnPc, has been outlined in the preceding paper.[1] Appraisal of known zinc–nitrogen bond distances in various coordination geometries suggests that the zinc(II) atom is too large to fit into the central hole of the phthalocyanato ligand. Of particular interest is the structure of the five-coordinate *n*-hexylamine adduct of phthalocyanatozinc(II).[2] The zinc(II) atom is displaced 0.48 Å from the basal plane of the phthalocyanato nitrogen atoms; the average phthalocyanato nitrogen–zinc bond distance is 2.06 Å. The Zn–N bond distances in five-coordinate porphyrin derivatives are slightly larger at 2.07 Å; the displacement of the zinc atom slightly smaller at 0.31–0.33 Å.[3,4] Hence ZnPc could be expected to provide an analogous example to the structure observed for *meso*-tetraphenylporphinatomanganese(II).[1] Our earlier studies of MnPc and FePc,[5] in addition to providing useful standards of reference for an analysis of thermal vibrations in the crystal, indicated that crystals of ZnPc could be expected to yield a data set containing a large number of high-resolution reflections. This expectation was met, and we report herein the molecular stereochemistry of ZnPc derived from measurements corresponding to a theoretical resolution[6] of 0.326 Å ($2\theta$ = 83.3) with Mo K$\alpha$ radiation.

## Experimental Section

ZnPc was prepared by a published procedure[7] and purified by vacuum sublimation. Single crystals, suitable for x-ray study, were grown by vacuum sublimation in quartz tubes at ~450 °C under a nitrogen atmosphere. Crystals used in the analysis were cut from larger needles. All measurements were derived from a specimen measuring 0.15 × 0.15 × 0.66 mm.

Preliminary photographic examination showed that ZnPc crystallized as the well-known $\beta$-polymorph. The space group $P2_1/a$ [$C_{2h}{}^5$, No. 14],[8] a nonstandard choice, was chosen to conform to earlier choices of unit cells for phthalocyanato derivatives.[9] Lattice constants, $a$ = 19.274 (5), $b$ = 4.8538 (15), $c$ = 14.553 (4) Å, and $\beta$ = 120.48 (2)° ($\lambda$ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at $\pm 2\theta$, given by the automatic centering routine supplied with the Syntex P$\bar{1}$ diffractometer. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C. The calculated density for two molecules per unit cell was 1.614 g/cm$^3$; the measured density was 1.62 g/cm$^3$.

X-ray intensity data were collected using graphite-monochromated Mo K$\alpha$ radiation on a computer-controlled four-circle diffractometer, using $\theta$–$2\theta$ scanning to a $2\theta$ limit of 83.3° ($(\sin\theta)/\lambda$ = 0.935 Å$^{-1}$). The scan range was 1.1° on either side of the K$\alpha_1$, K$\alpha_2$ doublet. Scan rates varied from 1.0 to 8.0°, with most reflections being measured at the slowest scan rate. Background counts were estimated from an analysis of the reflection profiles using a local modification of a program recently described.[10] Four standard reflections, measured every 50 reflections during data collection, displayed no trend with exposure to the x-ray beam. With the cited dimensions of the crystal and a linear absorption coefficient of 1.10 mm$^{-1}$, the error in intensity from neglect of absorption effects was seen to be less than 3%; this was confirmed by $\psi$ scans and no correction was applied. Intensity data were reduced and standard deviations calculated as described previously.[11] Data were retained as objectively observed if $F_o > 3\sigma(F_o)$, leading to 4515 unique observed data (56% of the theoretical number possible).

Atomic coordinates reported for CuPc[12] were used for the initial coordinates in the asymmetric unit of structure (one-half of the ZnPc molecule). Full-matrix least-squares refinement[13] converged smoothly using isotropic temperature factors for all atoms and standard values[14,15] for atomic form factors. Difference Fourier syntheses[16] gave electron density concentrations appropriately located for all hydrogen atom positions; these positions were idealized (C–H = 0.95 Å) with temperature factors fixed one unit higher than that of the associated carbon atom. Subsequent refinement used anisotropic temperature factors for all heavy atoms and fixed hydrogen contributors and was carried to convergence. The final parameter shifts were less than 10% of the estimated standard deviations during the last cycle. Final values of the discrepancy indices $R_1 = \Sigma[|F_o| -$

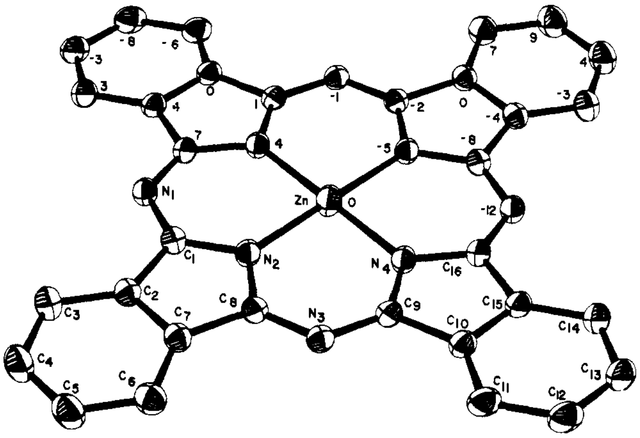

Figure 1. Computer-drawn model in perspective of the centrosymmetric ZnPc molecule as it exists in the crystal. On the lower half of the diagram the special symbol identifying each atom is shown. On the upper half of the figure, the symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the entire molecule.

**Table I.** Atom Coordinates in the Unit Cell

| Atom type | Coordinates$^a$ × $10^4$ | | |
|---|---|---|---|
| | $x$ | $y$ | $z$ |
| Zn | 0 | 0 | 0 |
| N(1) | −783 (1) | −5176 (3) | 716 (1) |
| N(2) | 345 (1) | −2027 (3) | 1345 (1) |
| N(3) | 1608 (1) | 268 (3) | 2524 (1) |
| N(4) | 992 (1) | 2242 (3) | 750 (1) |
| C(1) | −85 (1) | −4097 (4) | 1460 (1) |
| C(2) | 331 (1) | −4985 (4) | 2564 (1) |
| C(3) | 142 (1) | −6975 (5) | 3092 (2) |
| C(4) | 673 (1) | −7286 (5) | 4178 (2) |
| C(5) | 1370 (1) | −5688 (6) | 4721 (2) |
| C(6) | 1563 (1) | −3708 (5) | 4191 (2) |
| C(7) | 1030 (1) | −3392 (4) | 3101 (1) |
| C(8) | 1028 (1) | −1540 (4) | 2308 (1) |
| C(9) | 1590 (1) | 1980 (4) | 1798 (1) |
| C(10) | 2228 (1) | 3946 (4) | 2018 (1) |
| C(11) | 2969 (1) | 4514 (4) | 2926 (2) |
| C(12) | 3445 (1) | 6538 (5) | 2846 (2) |
| C(13) | 3194 (1) | 7969 (5) | 1897 (2) |
| C(14) | 2455 (1) | 7426 (4) | 989 (2) |
| C(15) | 1979 (1) | 5384 (4) | 1064 (1) |
| C(16) | 1198 (1) | 4276 (4) | 286 (1) |

[a] Numbers in parentheses are estimated standard deviations.

$|F_c|]/\Sigma|F_o|$ were 0.060, that of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$ was 0.073. The estimated standard deviation of an observation of unit weight was 1.48, with a final data/parameter ratio of 24.1. Refinements in which the Cr K$\alpha$ sphere data ($(\sin\theta)/\lambda \leqslant 0.437$ Å$^{-1}$) were eliminated were also carried to convergence. For this refinement $R_1 = 0.060$ and $R_2 = 0.057$. The structural parameters from this refinement were essentially identical with the first refinement; no bond distance varied by more than one estimated standard deviation. Refinements in which a disordered zinc atom (initial displacements out-of-plane of ±0.2 and ±0.3 Å) was assumed were also attempted. For both attempts, whenever the zinc atom coordinates were allowed to vary, the zinc atom gradually moved back to the origin.

Final difference Fourier syntheses were judged to have no significant features. A final listing of the observed and calculated structure factors (×10) is available.[17] Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure (derived from the refinement of the full data set) are listed in Tables I and II. Primed and unprimed symbols, $C_i'$ and $C_i$, represent atoms

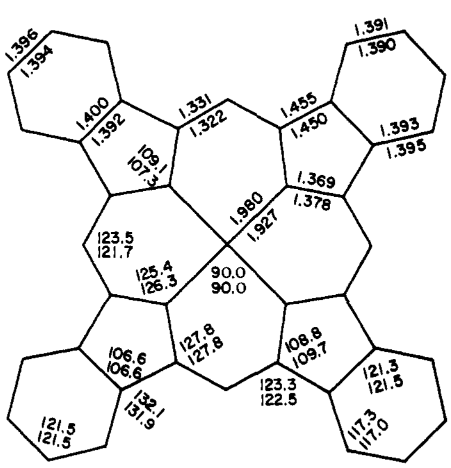

Figure 2. A formal diagram of the phthalocyanato skeleton. Values of the chemically distinctive classes of bond lengths (Å) and bond angles (deg) in ZnPc and FePc, averaged in agreement with $D_{4h}$ geometry, are entered on the diagram. The upper datum of each pairing is the value for ZnPc.

related by the center of symmetry at the origin (and the metal atom).

## Discussion

The numbering system employed in Tables I–V for the carbon and nitrogen atoms in the asymmetric unit of structure is displayed in Figure 1. This figure is a computer-drawn model[18] in perspective of the centrosymmetric ZnPc molecule. On the upper half of the centrosymmetric figure, the special symbol identifying each atom has been replaced by the value of the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the entire molecule. The pattern of displacements, although small, is quite similar to those observed for MnPc and FePc.[5] Individual units of the macrocycle, i.e., a pyrrole ring or a benzo ring, are planar to within 0.01 Å. The dihedral angle between the pyrrole ring and the associated benzo ring of an isoindole unit is less than 1.2°.

Individual bond parameters for the ZnPc molecule are given in Tables III and IV. Averaged values for chemically equivalent bond distances and angles for ZnPc and FePc (for subsequent consideration) are entered on Figure 2. The upper value of each pair of values refers to ZnPc.

The average Zn–N bond distance of 1.980 (2) Å is >0.04 Å longer than the metal-nitrogen distances observed for any other first row metallophthalocyanine derivative (see Table VI). However, the Zn–N bonds in ZnPc appear to be quite short when compared with Zn–N bond distances in other zinc complexes. A survey[21] of known Zn–N bond distances in complexes with a variety of coordination numbers and geometries reveals that for all cases, except tetrahedral, the observed Zn–N distances are greater than 2.06 Å (and frequently much greater). Even for the favored tetrahedral geometry, the observed Zn–N distances are generally greater than 2.00 Å (and again frequently much greater). The two tetrahedral complexes with Zn–N distances <2.00 Å were those with azide[22] or thiocyanate[23] as the tightly bound ligands; the Zn–N distances to the anionic ligand are 1.92–1.95 Å.

The 1.980-Å Zn–N distance for four-coordinate ZnPc is significantly decreased from the 2.06 to 2.07 Å values[25] observed in the five-coordinate phthalocyanato[2] and porphinato derivatives.[3,4] The decrease (0.08–0.09 Å) is substantially greater than the 0.044-Å decrease observed in four-coordinate MnTPP[1] vs. five-coordinate 1-methylimidazole-*meso*-tetraphenylporphinatomanganese(II);[24] the respective Mn–N distances are 2.084 and 2.128 Å.[25] It should be noted that the phthalocyanato core, although resistant to expansion in the

Table III. Bond Lengths in the Phthalocyanato Skeleton[a]

| Type[b] | Length, Å | Type | Length, Å | Type | Length, Å |
|---|---|---|---|---|---|
| Zn-N(2) | 1.980 (2) | N(4)-C(16) | 1.365 (2) | C(9)-C(10) | 1.459 (3) |
| Zn-N(4) | 1.979 (2) | C(1)-C(2) | 1.450 (2) | C(10)-C(11) | 1.396 (3) |
| N(1)-C(1) | 1.333 (2) | C(2)-C(3) | 1.393 (3) | C(10)-C(15) | 1.403 (3) |
| N(1)-C(16)′ | 1.332 (3) | C(2)-C(7) | 1.398 (3) | C(11)-C(12) | 1.387 (3) |
| N(2)-C(1) | 1.366 (2) | C(3)-C(4) | 1.389 (3) | C(12)-C(13) | 1.395 (4) |
| N(2)-C(8) | 1.372 (3) | C(4)-C(5) | 1.396 (4) | C(13)-C(14) | 1.391 (3) |
| N(3)-C(8) | 1.328 (2) | C(5)-C(6) | 1.396 (3) | C(14)-C(15) | 1.392 (3) |
| N(3)-C(9) | 1.330 (2) | C(6)-C(7) | 1.393 (3) | C(15)-C(16) | 1.452 (2) |
| N(4)-C(9) | 1.373 (2) | C(7)-C(8) | 1.461 (3) | | |

[a] The numbers in parentheses are the estimated standard deviations. [b] $C_i$ and $C_i'$ denote atoms related by the center of inversion.

Table IV. Bond Angles in the Phthalocyanato Skeleton[a]

| Angle | Value, deg | Angle | Value, deg | Angle | Value, deg |
|---|---|---|---|---|---|
| N(2)ZnN(4) | 89.0 (1) | C(1)C(2)C(7) | 106.8 (2) | N(4)C(9)C(10) | 108.7 (2) |
| N(4)ZnN(2)′ | 91.0 (1) | C(3)C(2)C(7) | 121.6 (2) | C(9)C(10)C(11) | 133.0 (2) |
| C(1)N(1)C(16)′ | 124.0 (2) | C(2)C(3)C(4) | 117.0 (2) | C(9)C(10)C(15) | 106.4 (1) |
| ZnN(2)C(1) | 124.5 (1) | C(3)C(4)C(5) | 121.8 (2) | C(11)C(10)C(15) | 120.7 (2) |
| ZnN(2)C(8) | 126.3 (1) | C(4)C(5)C(6) | 121.2 (2) | C(10)C(11)C(12) | 117.6 (2) |
| C(1)N(2)C(8) | 109.2 (1) | C(5)C(6)C(7) | 117.1 (2) | C(11)C(12)C(13) | 121.5 (2) |
| C(8)N(3)C(9) | 123.0 (2) | C(2)C(7)C(6) | 121.3 (2) | C(12)C(13)C(14) | 121.3 (2) |
| ZnN(4)C(9) | 126.3 (1) | C(2)C(7)C(8) | 106.5 (1) | C(13)C(14)C(15) | 117.3 (2) |
| ZnN(4)C(16) | 124.6 (1) | C(6)C(7)C(8) | 132.2 (2) | C(10)C(15)C(14) | 121.6 (2) |
| C(9)N(4)C(16) | 109.1 (1) | N(2)C(8)N(3) | 127.8 (2) | C(10)C(15)C(16) | 106.6 (1) |
| N(1)C(1)N(2) | 127.9 (2) | N(2)C(8)C(7) | 108.5 (2) | C(14)C(15)C(16) | 131.8 (2) |
| N(1)C(1)C(2) | 123.1 (2) | N(3)C(8)C(7) | 123.7 (2) | N(1)′C(16)N(4) | 128.0 (2) |
| N(2)C(1)C(2) | 109.0 (2) | N(3)C(9)N(4) | 127.6 (2) | N(1)′C(16)C(15) | 122.9 (2) |
| C(1)C(2)C(3) | 131.6 (2) | N(3)C(9)C(10) | 123.7 (2) | N(4)C(16)C(15) | 109.2 (2) |

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] $C_i$ and $C_i'$ denote atoms related by the center of inversion.

Table V. Root-Mean-Square Amplitudes of Vibration (Å)

| | Root mean square deviation × $10^3$ | | | |
|---|---|---|---|---|
| Atom | Min | Inter | Max | Γ, deg[a] |
| Zn | 151 (1) | 157 (0) | 219 (1) | 5 |
| N(1) | 145 (2) | 164 (2) | 172 (2) | 14 |
| N(2) | 143 (2) | 155 (2) | 173 (2) | 7 |
| N(3) | 152 (2) | 155 (2) | 168 (2) | 13 |
| N(4) | 142 (2) | 154 (2) | 173 (2) | 1 |
| C(1) | 144 (2) | 157 (2) | 166 (2) | 135 |
| C(2) | 149 (2) | 159 (2) | 170 (2) | 110 |
| C(3) | 149 (3) | 185 (2) | 201 (3) | 140 |
| C(4) | 147 (3) | 207 (3) | 224 (3) | 157 |
| C(5) | 151 (3) | 209 (3) | 222 (3) | 16 |
| C(6) | 155 (2) | 185 (3) | 204 (3) | 5 |
| C(7) | 147 (2) | 164 (2) | 170 (2) | 102 |
| C(8) | 148 (2) | 156 (2) | 159 (2) | 49 |
| C(9) | 146 (2) | 156 (2) | 162 (2) | 40 |
| C(10) | 148 (2) | 158 (2) | 172 (2) | 66 |
| C(11) | 152 (2) | 185 (2) | 197 (3) | 57 |
| C(12) | 149 (3) | 187 (3) | 231 (3) | 59 |
| C(13) | 145 (3) | 179 (3) | 230 (3) | 58 |
| C(14) | 147 (3) | 176 (2) | 202 (3) | 54 |
| C(15) | 144 (2) | 155 (2) | 176 (2) | 63 |
| C(16) | 139 (2) | 160 (2) | 165 (2) | 47 |

[a] Γ is the angle that the major axis of the vibrational ellipsoid makes with the normal to the least-squares plane through the phthalocyanine.

Table VI. Complexing Bond Lengths for Four-Coordinate Metallophthalocyanines

| Metallophthalocyanine | M-N distance, Å | Ref |
|---|---|---|
| MnPc | 1.938 (3) | *a* |
| FePc | 1.927 (1) | *a* |
| NiPc | ~1.83 | *b* |
| CuPc | 1.934 (6) | *c* |
| ZnPc | 1.980 (2) | *d* |
| PtPc | 1.98 (3) | *e* |
| SnPc | 2.25 (1) | *f* |

[a] Reference 5. [b] Reference 7. [c] Reference 12. [d] This work. [e] Reference 19. [f] Reference 20.

radial direction, can be expanded beyond the Ct$\cdots$N(≡M–N)[26] distance observed for ZnPc. Thus the phthalocyanato ligand, in order to accommodate the relatively large Sn(IV) atom in $Cl_2SnPc$,[27] expands so that Ct$\cdots$N(≡Sn–N) is 2.050 Å. Finally it should be observed that the thermal parameters (Tables II and V) of the zinc atom are consistent only with an atom centered or very nearly centered in the central hole of the ligand. In this respect, the ZnPc molecule is distinctly different from that observed for the MnTPP molecule. From the viewpoint of size and structure analogies, this difference seems surprising.

The changes in skeletal parameters accompanying the expansion of the phthalocyanato core can be noted with the aid of Figure 2. Averaged values of bond lengths and angles for ZnPc and FePc are entered in this figure; values of FePc[5] are representative of the contracted cores of the phthalocyanato derivatives entered in Table VI. Using $C_a$ and $C_b$ to represent the α- and β-carbon atoms of a pyrrole unit, $N_p$ for a pyrrole nitrogen atom, and $N_m$ for the azamethine atom, the following bond parameters are observed to change in ZnPc compared 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 azamethine 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]

**Acknowledgment.** We thank the National Institutes of Health (HL-15627) for partial support of this work and the Computing Center of the University of Notre Dame for computing time.

**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.

## References and Notes

(1) J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.* preceding paper in this issue.
(2) T. Kobayashi, T. Ashida, N. Uyeda, E. Suito, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **44**, 2095 (1971).
(3) D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3761 (1970).
(4) D. L. Cullen and E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **32**, 2259 (1976).
(5) J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, **15**, 1685 (1976).
(6) R. W. James, "The Optical Principles of the Diffraction of X-rays", G. Bell and Sons, London, England, 1965, p 400.
(7) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).
(8) N. F. M. Henry and K. Lonsdale, Eds., "International Tables for X-Ray Crystallography", 3rd ed, Vol. I, Kynoch Press, Birmingham, England, 1969, p 99.
(9) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937); R. P. Linstead and J. M. Robertson, *ibid.*, 1736 (1936); J. M. Robertson, *ibid.*, 615 (1935).
(10) R. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, **7**, 488 (1974).
(11) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).
(12) C. J. Brown, *J. Chem. Soc. A*, 2488 (1968).
(13) A local modification of ORFLS was employed: W. R. Busing, K. O. Martin, and H. A. Levy, "OR-FLS, A Fortran Crystallographic Least-Squares Program", Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962, Report No. ORNL-TM-305.
(14) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factor of the zinc atom from D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(15) Scattering factor for hydrogen from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) A locally modified version of ALFF was employed: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory, Iowa State University, Ames, Iowa, 1971, Report No. IS-2625.
(17) Supplementary material.
(18) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, Report No. ORNL-3794.
(19) C. J. Brown, *J. Chem. Soc. A*, 2494 (1968).
(20) M. K. Friedel, B. F. Hoskins, R. L. Martin, and S. A. Mason, *Chem. Commun.*, 400 (1970).
(21) Use was made of the series "Molecular Structures and Dimensions, Bibliography", O. Kennard and D. G. Watson, Ed., N. V. A. Oosthoek, Utrecht, The Netherlands.
(22) I. Agrell, *Acta Chem. Scand.*, **24**, 1247 (1970).
(23) F. Bigoli, A. Braibanti, M. A. Pellinghelli, and A. Tiripicchio, *Acta Crystallogr., Sect. B*, **29**, 2708 (1973).
(24) B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner, and W. R. Scheidt, *J. Am. Chem. Soc.*, **97**, 3247 (1975).
(25) These values are the averaged M–N distance in the equatorial plane.
(26) Ct is the symbol used for the center of the macrocyclic hole.
(27) D. Rogers and R. S. Osborn, *Chem. Commun.*, 840 (1971).
(28) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 6689 (1972).

---

# 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 = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$]

**Raymond G. Teller,[1a] Richard G. Finke,[1b] James P. Collman,[1b] Henry B. Chin,[1a] and Robert Bau*[1a,c]**

*Contribution from the Departments of Chemistry, University of Southern California, Los Angeles, California 90007, and Stanford University, Stanford, California 94305.*
*Received August 12, 1976*

**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 ex-