

Fig. 2. Stereoscopic packing diagram for $[\text{Ni}\{\text{NCH}_3(\text{CH}_2\text{COO})_2\} \cdot (\text{D}_2\text{O})_3] \cdot \text{D}_2\text{O}$ along the a axis with the b axis vertical.

The orientation of the protons on the methyl group provides minimal overlap with the protons on nearby C(1) and C(3) methylene carbon atoms. The average internal hydrogen-bond distance for hydrogen atoms attached to carbon is 0.94 Å, and 0.81 Å for hydrogen atoms attached to oxygen.

The equipment used in this study was funded in part by the National Science Foundation, grant No. CHE79-007027. We are grateful to Diane C. Fisher, Frederick J. Hollander, D. H. Templeton and Kenneth N. Raymond for their assistance.

References

ALBERTSSON, J. & OSKARSSON, Å. (1968). *Acta Chem. Scand.* **22**, 1700–1702.

ALBERTSSON, J. & OSKARSSON, Å. (1974). *Acta Chem. Scand. Ser. A*, **28**, 347–355.

BOMBIERI, G., FORSELLINI, E., TOMAT, G., MAGON, L. & GRAZIANI, R. (1974). *Acta Cryst.* **B30**, 2659–2663.

CORRADI, A. B., PALMIERI, C. G., NARDELLI, M., PELLINGHELLI, M. A. & VIDONI TANI, M. E. (1973). *J. Chem. Soc. Dalton Trans.* pp. 655–658.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KRAMARENKO, F. G., POLYNOVA, T. N., PORAI-KOSHITS, M. A., CHALYI, V. P. & MITROFANOVA, N. D. (1973). *J. Struct. Chem. (USSR)*, **14**, 1043–1044.

LEGG, J. I. & COOKE, D. W. (1966). *Inorg. Chem.* **5**, 594–601.

MAMMANO, N. J., TEMPLETON, D. H. & ZALKIN, A. (1977). *Acta Cryst.* **B33**, 1251–1254.

MOOTZ, D. & WUNDERLICH, H. (1980a). *Acta Cryst.* **B36**, 445–447.

MOOTZ, D. & WUNDERLICH, H. (1980b). *Acta Cryst.* **B36**, 721–722.

MOOTZ, D. & WUNDERLICH, H. (1980c). *Acta Cryst.* **B36**, 1189–1191.

NARDIN, G., RANDACCIO, L., BONOMO, R. P. & RIZZARELLI, E. (1980). *J. Chem. Soc. Dalton Trans.* pp. 369–375.

OSKARSSON, Å. (1971). *Acta Chem. Scand.* **25**, 1206–1216.

PODDER, A., DATTAGUPTA, J. K. & SAHA, N. N. (1979). *Acta Cryst.* **B35**, 53–56.

SINKHA, U. CH., KRAMARENKO, F. G., POLYNOVA, T. N., PORAI-KOSHITS, M. A. & MITROFANOVA, N. D. (1975). *J. Struct. Chem. (USSR)*, **16**, 131.

Structure Determination Package User's Guide (1982). B. A. FRENZ & Associates Inc. College Station, TX 77840.

Acta Cryst. (1985). **C41**, 671–673

Redetermination of the Structure of μ -Oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] at 122 K, $[\text{Fe}_2\text{O}(\text{C}_{44}\text{H}_{28}\text{N}_4)_2]$

BY PAUL N. SWEPSTON AND JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, IL 60201, USA

(Received 27 August 1984; accepted 19 November 1984)

Abstract. $M_r = 1353.2$, orthorhombic, $C2cb$ (C_{2v}^{17}), $a = 15.094$ (4), $b = 24.938$ (7), $c = 17.825$ (4) Å, $V = 6709.5$ Å³, $Z = 4$, crystallographically imposed C_2 molecular symmetry, $D_x = 1.34$ g cm⁻³, Mo $K\alpha$, $\lambda(K\alpha_1) = 0.7093$ Å, graphite monochromator, $\mu(\text{Mo } K\alpha) = 4.86$ cm⁻¹, $F(000) = 2802.4$, $T = 122$ K, $R(F^2) = 0.093$ for 11 416 unique observed reflections. Structural parameters derived from an extensive low-temperature data set are presented. The previously reported room-temperature structure [Hoffman, Collins, Day, Fleischer, Srivastava & Hoard (1972). *J. Am. Chem. Soc.* **94**, 3620–3626] is confirmed and improved.

Introduction. The structure of μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] was previously de-

termined (Fleischer & Srivastava, 1969; Hoffman *et al.*, 1972). Recent theoretical interest in this and other oxo-bridged molecules (Tatsumi, Hoffmann & Whangbo, 1980; Tatsumi & Hoffmann, 1981) prompted us to collect an extensive low-temperature data set for an experimental charge-density investigation. We were unable to produce a reasonable description of the valence electron density distribution from this study, but nonetheless we derived highly accurate structural parameters.

Experimental. The chosen aspect of space group C_{2v}^{17} was that of previous investigators (Fleischer & Srivastava, 1969) and is $C2cb$ (equivalent positions: $0,0,0; \frac{1}{2}, \frac{1}{2}, 0 + x, y, z; x, \bar{y}, \bar{z}; x, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z$). The origin has been fixed by x of Fe. Bounding faces of the

Table 1. Positional parameters and B_{eq} for μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)]
$$B_{eq} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | $B_{eq}(\text{\AA}^2)$ |
|-------|---------------|---------------|---------------|------------------------|
| Fe | -0.00495 | 0.505617 (11) | 0.401708 (16) | 1.2 |
| O(1) | -0.00100 (24) | $\frac{1}{2}$ | $\frac{1}{2}$ | 1.5 |
| N(1) | -0.06715 (14) | 0.436737 (78) | 0.36219 (12) | 1.5 |
| N(2) | 0.11348 (14) | 0.471571 (75) | 0.36626 (11) | 1.4 |
| N(3) | 0.05542 (14) | 0.579765 (77) | 0.38462 (12) | 1.5 |
| N(4) | -0.12587 (14) | 0.544079 (78) | 0.38549 (11) | 1.5 |
| C(1) | -0.15707 (17) | 0.42812 (10) | 0.35402 (15) | 1.6 |
| C(2) | -0.17221 (18) | 0.37399 (11) | 0.32843 (15) | 2.0 |
| C(3) | -0.09265 (17) | 0.349615 (98) | 0.32397 (15) | 1.8 |
| C(4) | -0.02718 (16) | 0.388577 (92) | 0.34574 (14) | 1.6 |
| C(5) | 0.06404 (16) | 0.378681 (93) | 0.34644 (13) | 1.6 |
| C(6) | 0.12887 (16) | 0.417986 (98) | 0.35557 (14) | 1.6 |
| C(7) | 0.22278 (17) | 0.40829 (10) | 0.34849 (16) | 1.9 |
| C(8) | 0.26320 (17) | 0.45646 (10) | 0.35394 (16) | 1.9 |
| C(9) | 0.19534 (16) | 0.495738 (97) | 0.36524 (14) | 1.6 |
| C(10) | 0.21127 (17) | 0.550890 (96) | 0.37195 (14) | 1.5 |
| C(11) | 0.14494 (17) | 0.58948 (10) | 0.38193 (15) | 1.6 |
| C(12) | 0.16198 (18) | 0.645874 (99) | 0.39244 (16) | 2.1 |
| C(13) | 0.08206 (18) | 0.669646 (96) | 0.40282 (17) | 2.0 |
| C(14) | 0.01599 (16) | 0.628633 (87) | 0.39795 (14) | 1.6 |
| C(15) | -0.07511 (17) | 0.637432 (92) | 0.40629 (14) | 1.7 |
| C(16) | -0.14040 (17) | 0.59737 (10) | 0.40120 (15) | 1.7 |
| C(17) | -0.23327 (17) | 0.60667 (10) | 0.41097 (16) | 2.0 |
| C(18) | -0.27482 (17) | 0.55909 (10) | 0.40204 (16) | 1.9 |
| C(19) | -0.20740 (16) | 0.51981 (10) | 0.38422 (14) | 1.6 |
| C(20) | -0.22389 (17) | 0.46593 (10) | 0.36799 (14) | 1.6 |
| C(21) | 0.09384 (17) | 0.322008 (97) | 0.33268 (15) | 1.8 |
| C(22) | 0.08931 (29) | 0.28418 (12) | 0.38876 (18) | 3.6 |
| C(23) | 0.11560 (35) | 0.23154 (13) | 0.37406 (23) | 4.6 |
| C(24) | 0.14649 (26) | 0.21700 (11) | 0.30519 (21) | 3.4 |
| C(25) | 0.15092 (22) | 0.25473 (11) | 0.24916 (21) | 2.9 |
| C(26) | 0.12426 (20) | 0.30711 (10) | 0.26245 (16) | 2.3 |
| C(27) | 0.30534 (17) | 0.569394 (96) | 0.36820 (15) | 1.6 |
| C(28) | 0.36139 (20) | 0.56319 (12) | 0.42942 (16) | 2.5 |
| C(29) | 0.44961 (20) | 0.57805 (14) | 0.42474 (19) | 2.9 |
| C(30) | 0.48250 (19) | 0.59997 (12) | 0.35912 (19) | 2.7 |
| C(31) | 0.42786 (21) | 0.60582 (14) | 0.29856 (18) | 3.1 |
| C(32) | 0.33939 (19) | 0.59079 (13) | 0.30273 (16) | 2.7 |
| C(33) | -0.10411 (18) | 0.69344 (10) | 0.42143 (15) | 1.9 |
| C(34) | -0.10922 (29) | 0.73045 (12) | 0.36446 (19) | 3.3 |
| C(35) | -0.13394 (30) | 0.78342 (13) | 0.37886 (21) | 3.8 |
| C(36) | -0.15268 (26) | 0.79945 (12) | 0.45004 (21) | 3.4 |
| C(37) | -0.14687 (36) | 0.76302 (16) | 0.50759 (22) | 4.9 |
| C(38) | -0.12405 (33) | 0.71000 (14) | 0.49310 (18) | 4.1 |
| C(39) | -0.31804 (17) | 0.44694 (11) | 0.36585 (14) | 1.8 |
| C(40) | 0.15552 (18) | 0.40351 (11) | 0.08990 (15) | 2.0 |
| C(41) | 0.06839 (19) | 0.38522 (12) | 0.09199 (18) | 2.5 |
| C(42) | 0.00672 (20) | 0.41057 (12) | 0.13745 (17) | 2.7 |
| C(43) | 0.03226 (18) | 0.45374 (12) | 0.18151 (16) | 2.4 |
| C(44) | 0.11993 (17) | 0.47138 (11) | 0.18019 (14) | 1.9 |

wedge-shaped crystal: {002}, {020}, (201), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}\bar{1}$); crystal vol. = 0.048 mm³; Picker automatic diffractometer; 17 reflections (2θ range = 27–40°) used for measuring lattice parameters; analytical absorption correction applied with a transmission-factor range of 0.86–0.89; data collected: +*h*, +*k*, +*l* with $(\sin\theta)/\lambda_{\max} = 0.925 \text{ \AA}^{-1}$ and -*h*, -*k*, -*l* with $(\sin\theta)/\lambda_{\max} = 0.305 \text{ \AA}^{-1}$; six standard reflections (915, 208, 134, 14, 0, 0, 0, 10, 151) measured at 100-reflection intervals showed no significant variation in intensity; 11 973 reflections measured; 11 416 unique reflections; all measured reflections considered observed; solution by direct methods by use of MULTAN80 (Main *et al.*, 1980). Determination of the polar direction for the chosen crystal was made after a full isotropic refinement based on *F* with reflections having $F_o^2 \geq 3\sigma(F_o^2)$ and with no anomalous dispersion. Solution *A* was obtained by including anomalous

dispersion and continuing the isotropic refinement. The residuals for solution *A* were $R = 0.065$ and $wR = 0.079$. Solution *B* was obtained by including anomalous dispersion, reversing the signs for the atomic coordinates, and proceeding with the refinement. The residuals for solution *B* were $R = 0.063$ and $wR = 0.077$. Examination of the 20 Friedel pairs of reflections showing the largest differences between $F_o(hkl)$ and $F_o(\bar{h}\bar{k}\bar{l})$ indicated that solution *B* correctly predicted the sign of such differences in all cases. Thus solution *B* is the correct model. Final refinement cycles based on F^2 magnitudes; H-atom positions derived with the assumption of idealized geometries (C–H = 0.95 Å); all non-H atoms refined anisotropically; $w = 1/\sigma^2(F^2)$; $R(F^2) = 0.093$; $wR(F^2) = 0.120$; $S(F^2) = 1.12$; $R(F) = 0.055$ based on 6574 reflections for which $F_o^2 \geq 3.0\sigma(F_o^2)$; max. Δ/σ 0.16 in final cycle of refinement; in final difference electron density synthesis max. and min. heights 0.8 (3) and -0.8 (3) e Å⁻³; atomic scattering factors for non-H atoms those of Cromer & Waber (1974); for H those of Stewart, Davidson & Simpson (1965); an anomalous-dispersion correction (Ibers & Hamilton, 1964) for the Fe atom was applied using values of f' and f'' of Cromer & Waber (1974); all calculations performed using computer programs previously described (Casella, Silver & Ibers, 1984).

Discussion. Fractional coordinates for the non-H atoms of μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] are presented as Table 1. The molecular geometry, atom-numbering scheme, and averaged

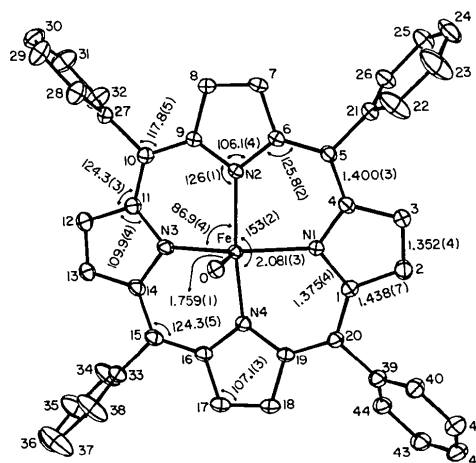


Fig. 1. Drawing of the crystallographically unique fragment of μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron(III)] (50% probability thermal ellipsoids) along with the atom-numbering scheme and averaged bond lengths (Å) and angles (°). An e.s.d. in parentheses is the larger of that estimated for a single observation from the inverse matrix or from the values averaged. H atoms have been omitted for clarity.

metrical parameters for the porphyrin core are displayed in Fig. 1.* The intrinsic fourfold symmetry of the porphyrin skeleton is reflected in the small values for the e.s.d.'s of the averaged parameters.

The previously reported structure (Hoffman *et al.*, 1972) is confirmed. There is no significant difference between the room-temperature and low-temperature (122 K) geometries, but this report presents a twofold increase in accuracy for the structural parameters of this molecule.

We acknowledge the support of the US National Institutes of Health (Grant HL-13157).

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom positions, and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39917 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1985). C41, 673–678

The Structures and Solid-State and Solution ^{113}Cd NMR of Diaquabis(*p*-chlorobenzoato)-cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{H}_2\text{O})_2]$ (A), Diaquabis(*p*-nitrobenzoato)cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$ (B), and Aquabis(*p*-chlorobenzoato)bis(pyridine)cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]$ (C)

BY P. F. RODESILER

Department of Chemistry, Columbia College, Columbia, South Carolina 29203, USA

AND E. A. H. GRIFFITH, N. G. CHARLES AND E. L. AMMA*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, USA

(Received 21 May 1984; accepted 26 November 1984)

Abstract. (A) $M_r = 459.55$, monoclinic, $C2/c$, $a = 25.904$ (9), $b = 5.371$ (2), $c = 12.049$ (7) Å, $\beta = 107.02$ (4)°, $V = 1603$ (2) Å³, $Z = 4$, $D_m = 1.89$ (2), $D_x = 1.90$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 17.1$ cm⁻¹, $F(000) = 904$, $T \sim 298$ K, $R(\text{final}) = 0.049$ for 2228 reflections. (B) $M_r = 480.66$, monoclinic, $C2/c$, $a = 26.415$ (3), $b = 5.416$ (1), $c = 12.179$ (4) Å, $\beta = 90.52$ (3)°, $V = 2514$ (3) Å³, $Z = 4$, $D_m = 1.95$ (2), $D_x = 1.96$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 14.0$ cm⁻¹, $F(000) = 952$, $T \sim 298$ K, $R(\text{final}) = 0.039$ for 2378 reflections. (C) $M_r = 599.8$, monoclinic, $C2/c$, $a = 16.908$ (7), $b = 6.058$ (2), $c = 24.547$ (2) Å, $\beta = 90.52$ (3)°, $V = 2514$ (3) Å³, $Z = 4$, $D_m = 1.59$ (2), $D_x = 1.59$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 11.1$ cm⁻¹, $F(000) = 1200$, $T \sim 298$ K, $R(\text{final}) = 0.036$ for 3681 reflections. The structures of (A) and

(B) are made up of distorted six-coordinate Cd^{II} moieties, intermediate in metal-coordination geometry between octahedral and trigonal prismatic, separated by ordinary van der Waals distances. The crystal structure of (C) is made up of seven-coordinate pentagonal bipyramidal Cd^{II} separated by ordinary van der Waals distances. The solid-state ^{113}Cd NMR of (A) and (B) consists of a single line at +24 p.p.m., relative to the Cd(ClO₄)₂ standard. The solid-state ^{113}Cd NMR of (C) and the analogous adduct of (B) consists of a single line at +30 and +29 p.p.m. respectively. The methanol solution ^{113}Cd NMR spectra of (A) and (B) consist of a single line at -51 p.p.m. and -53 p.p.m. respectively. These results for all-oxygen coordination are interpreted as the positive values arising from the distorted six-coordinate Cd^{II} and the negative values correspond to pentagonal bipyramidal seven-oxygen-coordinated metal species in solution.

* To whom correspondence should be addressed.

References

- CASELLA, L., SILVER, M. E. & IBERS, J. A. (1984). *Inorg. Chem.* **23**, 1409–1418.
- CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- FLEISCHER, E. B. & SRIVASTAVA, T. S. (1969). *J. Am. Chem. Soc.* **91**, 2403–2405.
- HOFFMAN, A. B., COLLINS, D. M., DAY, V. W., FLEISCHER, E. B., SRIVASTAVA, T. S. & HOARD, J. L. (1972). *J. Am. Chem. Soc.* **94**, 3620–3626.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TATSUMI, K. & HOFFMANN, R. (1981). *J. Am. Chem. Soc.* **103**, 3328–3341.
- TATSUMI, K., HOFFMANN, R. & WHANGBO, M.-H. (1980). *J. Chem. Soc. Chem. Commun.* pp. 509–511.