

between  $-0.50$  and  $0.76 \text{ e} \text{ \AA}^{-3}$ . The final atomic parameters are given in Table 1.\* The principal interatomic distances and angles are given in Table 2. The view showing the structure of two crystallographically independent anions is shown in Fig. 1 and the packing of the crystal in Fig. 2.

**Related literature.** This redetermination has yielded e.s.d.'s about half those achieved by Katti *et al.* (1981). The structures of phosphoenolpyruvic acid (PEP) and of the anions  $\text{PEP}^-$ ,  $\text{PEP}^{2-}$  and  $\text{PEP}^{3-}$  are therefore now known to similar precision since the structures of two polymorphic forms of cyclohexylammonium phosphoenolpyruvate were given by Weichsel & Lis (1989a) and that of the potassium salt by Lis (1987) while phosphoenolpyruvic acid itself has been described by Weichsel & Lis (1989b).

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53393 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

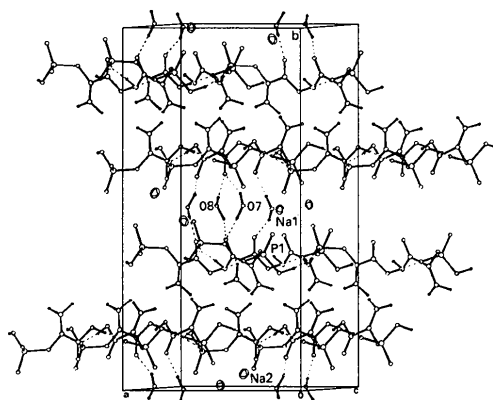


Fig. 2. Packing arrangement and hydrogen bonds in sodium phosphoenolpyruvate hydrate.

#### References

- KATTI, S. K., HOSUR, M. V. & VISWAMITRA, M. A. (1981). *Acta Cryst.* B37, 834–838.  
 LIS, T. (1987). *Acta Cryst.* C43, 1898–1900.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 WEICHSEL, A. & LIS, T. (1989a). *Acta Cryst.* C45, 1177–1180.  
 WEICHSEL, A. & LIS, T. (1989b). *Carbohydr. Res.* 194, 63–70.

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## Structure of (2,3,7,8,12,13,17,18-Octaethylporphinato)copper(II)

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**Abstract.**  $[\text{Cu}(\text{C}_{36}\text{H}_{44}\text{N}_4)]$ ,  $M_r = 596.3$ , triclinic,  $P\bar{1}$ ,  $a = 13.314(5)$ ,  $b = 13.392(5)$ ,  $c = 4.805(3) \text{ \AA}$ ,  $\alpha = 92.42(4)^\circ$ ,  $\beta = 93.38(4)^\circ$ ,  $\gamma = 113.08(1)^\circ$ ,  $V = 784.8 \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 1.26 \text{ g cm}^{-3}$ ,  $D_m = 1.25 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 7.25 \text{ cm}^{-1}$ ,  $F(000) = 317$ ,  $T = 293 \text{ K}$ ,  $R = 0.055$  for 2166 unique observed reflections.

**Experimental.** Crystals of the title compound were prepared by slow evaporation of a chloroform solution.  $D_m$  was measured by flotation in  $\text{CCl}_4/\text{hexane}$ . A purple, air-stable crystal with approximate dimensions of  $0.41 \times 0.05 \times 0.04 \text{ mm}$  was mounted on the end of a glass fiber. All measurements were per-

formed with graphite-monochromated Mo  $K\alpha$  radiation on an Enraf–Nonius CAD-4 diffractometer. Intensity data were measured by  $\theta$ – $2\theta$  scans at scan rates of  $2$ – $16^\circ \text{ min}^{-1}$ . Data were collected to a maximum  $2\theta$  of  $58.7^\circ$  and standard  $\theta$ – $2\theta$  CAD-4 moving-crystal moving-counter background measurements were used. 25 reflections used for measuring lattice parameters  $9.23 < \theta < 12.17^\circ$ . Range of  $hkl$ :  $-16 \rightarrow 16$ ,  $-16 \rightarrow 16$ ,  $-6 \rightarrow 6$ , 9147 reflections measured, 4305 unique, 2166 with  $I > 3\sigma(I)$  considered observed. Merging  $R = 0.031$  for 4297 duplicates. Four standard reflections, 9.7% intensity decrease. The data were corrected for background (profile analysis), Lorentz, polarization, crystal decay and absorption effects using the Blessing (1987) suite for data reduction. Empirical absorption correction was

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Table 1. Fractional coordinates and equivalent isotropic thermal parameters, with the e.s.d.'s of the least significant digits given in parentheses

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cu	0.0000	0.0000	0.0000	3.77
N(1)	0.06125 (25)	-0.06728 (26)	0.2913 (7)	3.61
N(2)	0.12963 (26)	0.14091 (27)	0.0816 (7)	3.78
C(1)	0.0170 (3)	-0.1723 (3)	0.3690 (8)	3.78
C(2)	0.0882 (4)	-0.1898 (4)	0.5840 (9)	4.25
C(3)	0.1744 (3)	-0.0936 (4)	0.6412 (9)	4.17
C(4)	0.1586 (3)	-0.0168 (3)	0.4591 (9)	3.94
C(5)	0.2291 (4)	0.0895 (4)	0.4468 (9)	4.08
C(6)	0.2188 (3)	0.1630 (3)	0.2686 (9)	3.95
C(7)	0.2972 (3)	0.2732 (3)	0.2536 (10)	4.40
C(8)	0.2555 (3)	0.3195 (3)	0.0615 (10)	4.53
C(9)	0.1506 (3)	0.2361 (3)	-0.0542 (9)	3.96
C(10)	0.0817 (3)	0.2496 (3)	-0.2553 (9)	4.18
C(11)	0.0687 (4)	-0.2967 (4)	0.7054 (10)	5.20
C(12)	0.1165 (6)	-0.3634 (5)	0.5420 (14)	7.46
C(13)	0.2739 (4)	-0.0676 (4)	0.8427 (10)	5.33
C(14)	0.3688 (5)	-0.0755 (6)	0.7089 (15)	7.78
C(15)	0.4076 (4)	0.3213 (4)	0.4214 (11)	5.38
C(16)	0.4903 (4)	0.2837 (5)	0.2973 (14)	7.01
C(17)	0.3025 (4)	0.4344 (4)	-0.0315 (11)	5.22
C(18)	0.2574 (5)	0.5078 (4)	0.1158 (13)	6.65

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the Ca(oep) molecule

Cu—N(1)	1.996 (3)	C(1)—C(2)	1.449 (6)
Cu—N(2)	1.999 (3)	C(4)—C(3)	1.445 (6)
N(1)—C(1)	1.373 (5)	C(6)—C(7)	1.443 (6)
N(1)—C(4)	1.390 (5)	C(9)—C(8)	1.463 (6)
N(2)—C(6)	1.371 (5)	C(2)—C(11)	1.502 (6)
N(2)—C(9)	1.393 (5)	C(3)—C(13)	1.508 (6)
C(1)—C(10')	1.378 (6)	C(7)—C(15)	1.516 (6)
C(4)—C(5)	1.370 (6)	C(8)—C(17)	1.515 (6)
C(5)—C(6)	1.373 (6)	C(11)—C(12)	1.504 (7)
C(9)—C(10)	1.359 (6)	C(13)—C(14)	1.489 (7)
C(2)—C(3)	1.352 (6)	C(15)—C(16)	1.520 (7)
C(7)—C(8)	1.342 (6)	C(17)—C(18)	1.511 (7)
N(1)—Cu—N(2)	90.1 (1)	N(2)—C(6)—C(5)	123.7 (4)
N(1)—Cu—N(2')	89.9 (1)	N(2)—C(6)—C(7)	110.6 (4)
C(1)—N(1)—C(4)	105.4 (3)	C(5)—C(6)—C(7)	125.7 (4)
C(6)—N(2)—C(9)	105.6 (3)	C(8)—C(7)—C(6)	107.5 (4)
N(1)—C(1)—C(10)	124.0 (4)	C(8)—C(7)—C(15)	128.5 (4)
N(1)—C(1)—C(2)	110.8 (4)	C(6)—C(7)—C(15)	123.9 (4)
C(10)—C(1)—C(2)	125.3 (4)	C(7)—C(8)—C(9)	106.9 (4)
C(3)—C(2)—C(1)	106.5 (4)	C(7)—C(8)—C(17)	129.5 (4)
C(3)—C(2)—C(11)	128.3 (4)	C(9)—C(8)—C(17)	123.6 (4)
C(1)—C(2)—C(11)	125.1 (4)	C(10)—C(9)—N(2)	124.8 (4)
C(2)—C(3)—C(4)	107.4 (4)	C(10)—C(9)—C(8)	125.8 (4)
C(2)—C(3)—C(13)	128.4 (4)	N(2)—C(9)—C(8)	109.3 (4)
C(4)—C(3)—C(13)	124.1 (4)	C(9)—C(10)—C(1)	126.9 (4)
C(5)—C(4)—N(1)	124.3 (4)	C(2)—C(11)—C(12)	112.5 (4)
C(5)—C(4)—C(3)	125.8 (4)	C(14)—C(13)—C(3)	113.3 (4)
N(1)—C(4)—C(3)	109.9 (4)	C(7)—C(15)—C(16)	111.9 (4)
C(4)—C(5)—C(6)	127.2 (4)	C(18)—C(17)—C(8)	112.4 (4)

based on azimuthal ( $\varphi$ ) scans of 5 reflections. Solved by direct methods: *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares minimized  $w(\Delta F)^2$  with a total of 187 variables. The H atoms were positioned according to idealized geometry (C—H = 0.95  $\text{\AA}$ ) and given isotropic  $B$ 's of  $1.3 \times B$  of attached atom. All non-H atoms refined anisotropically.  $R = 0.055$ ,

$wR = 0.059$ ,  $S = 1.16$ . Weighting scheme  $w = 1/[\sigma(F_o)]^2$ . Final difference peak 0.64  $e \text{\AA}^{-3}$  near Cu. Final  $(\Delta/\sigma)_{\max} = 0.03$ . Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). A locally modified version of *ALLS* (Lapp & Jacobson, 1979) used for structure refinement and *ORFFE* (Busing, Martin & Levy, 1964) for structural parameters with e.s.d.'s. Table 1 gives atomic coordinates and Table 2 bond distances and angles.\* Fig. 1 gives the atomic numbering of the crystallographically independent half-molecule and a perspective drawing of the molecule.

**Related literature.** Crystalline Cu(oep) is isomorphous with a recently reported polymorph of Ni(oep) (Brennan, Scheidt & Shelnut, 1988) and with Fe(oep) (Strauss, Silver, Long, Thompson, Hudgens, Spartalian & Ibers, 1985). In common with these structures, the molecules of Cu(oep) pack with an extended  $\pi$ - $\pi$  interaction along the  $c$  axis. Like these earlier derivatives, the M—N bond that is within the aggregate stack is the longer of the two unique Cu—N distances. However, in the present case, the differences in the Cu—N distances are not statistically significant. The average 1.998 (2)  $\text{\AA}$  distance in Cu(oep) is comparable to the Cu—N distances observed in other planar porphinatocopper(II) derivatives (Moustakali & Tulinsky, 1973; Song, Reed & Scheidt, 1989).

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53401 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

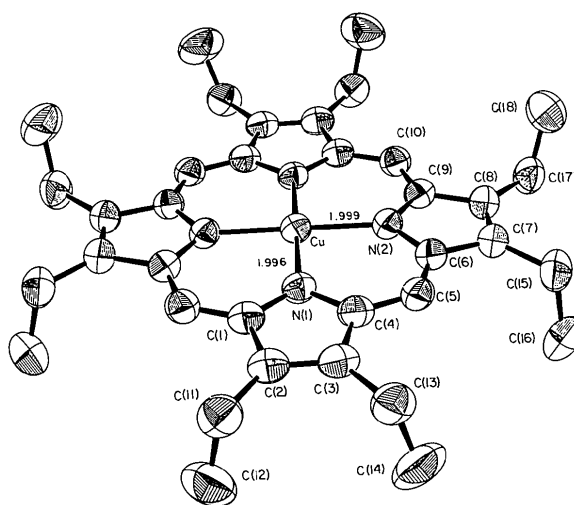


Fig. 1. ORTEP (Johnson, 1976) diagram and numbering scheme for all heavy atoms. 50% probability surfaces.

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### References

- BLESSING, R. H. (1987). *Cryst. Rev.* **1**, 3–58.  
 BRENNAN, T. D., SCHEIDT, W. R. & SHELNUTT, J. A. (1988). *J. Am. Chem. Soc.* **110**, 3919–3924.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.  
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 LAPP, R. L. & JACOBSON, R. A. (1979). *ALLS. A Generalized Crystallographic Least Squares Program*. National Technical Information Services IS-4708 UC-4, Springfield, Virginia, USA.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MOUSTAKALI, I. & TULINSKY, A. (1973). *J. Am. Chem. Soc.* **95**, 6811–6815.  
 SONG, H., REED, C. A. & SCHEIDT, W. R. (1989). *J. Am. Chem. Soc.* **111**, 6865–6868.  
 STRAUSS, S. H., SILVER, M. E., LONG, K. M., THOMPSON, R. G., HUDGENS, R. A., SPARTALIAN, K. & IBERS, J. A. (1985). *J. Am. Chem. Soc.* **107**, 4207–4215.

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## Structure Determination of a Nickel Croconate Complex: $[\text{Ni}(\text{OH}_2)(\text{C}_5\text{O}_5)(\text{C}_3\text{H}_4\text{N}_2)_3]\text{H}_2\text{O}$

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**Abstract.** Aqua(4,5-dihydroxy-4-cyclopentene-1,2,3-trionato)tris(imidazole)nickel(II) monohydrate,  $\text{C}_{14}\text{H}_{14}\text{N}_6\text{NiO}_6\cdot\text{H}_2\text{O}$ ,  $M_r = 439.0$ , monoclinic,  $P2_1/c$ ,  $a = 8.581$  (1),  $b = 9.442$  (1),  $c = 22.583$  (2) Å,  $\beta = 93.06$  (1)°,  $V = 1827.1$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.596$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.11$  mm<sup>-1</sup>,  $F(000) = 904$ ,  $T = 293$  K. Full-matrix least-squares refinement based on 2761 reflections led to  $R$  and  $wR$  values of 0.034 and 0.037 respectively. The coordination of the metal is ensured by three imidazole groups, one water molecule and one croconate molecule acting as chelating ligand.

**Experimental.** Blue-green parallelepiped crystals obtained from reaction in water of  $\text{NiCl}_2$ ,  $6\text{H}_2\text{O}$  (0.5 mmol), imidazole (0.5 mmol) and sodium croconate  $\text{C}_5\text{O}_5\text{Na}_2$ ,  $3\text{H}_2\text{O}$  (0.25 mmol). Analysis: calculated C 38.30, H 3.67, N 19.14%; found C 37.91, H 3.37, N 18.66%. Crystal  $0.40 \times 0.075 \times 0.05$  mm, sealed on a glass fiber, CAD-4 diffractometer, graphite-monochromated  $\text{Mo } K\alpha$ , cell parameters from a least-squares fitting of 25 reflections with  $\theta$  between 7.2 and 14.7°, 4215 reflections measured, using  $\omega/2\theta$  scan for  $2\theta$  from 3 to 54° ( $h$  0 to 10,  $k$  0 to 12,  $l$  -28 to 28), scan range  $(0.90 + 0.35\tan\theta)^\circ$ . Intensities of three reflections (008, 040, 304) measured every 2 h during data collection showed a decay

of 5%. Corrections for  $L_p$  and linear decay. Empirical absorption corrections (North, Phillips & Mathews, 1968):  $T_{\min} = 0.90$ ,  $T_{\max} = 1.00$  and merging equivalent reflections  $0kl$  and  $0k\bar{l}$ ;  $R_{\text{int}} = 0.019$ . Heavy-atom method followed by Fourier and least-squares techniques using 2761 reflections having  $F_o^2 > 2\sigma(F_o^2)$  based on counting statistics. Full-matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$ , with anisotropic thermal parameters for all non-H atoms, all H atoms observed on a Fourier difference map, H atoms from water molecules allowed to vary, other H atoms in constrained geometry (C—H = N—H = 0.97 Å).

Isotropic  $U_H$  allowed to vary (one for each H from the water molecule, one for all other H atoms).  $R = 0.034$ ,  $wR = 0.037$ , 268 variables, unit weights. † Mean and max. parameter shifts  $0.009\sigma$  and  $0.078\sigma$ , respectively. Max. and min. height in final  $\Delta F$  map 0.79 and  $-0.36$  e Å<sup>-3</sup>. Scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974, Vol IV, pp. 99–101, 149) and from Stewart, Davidson & Simpson (1965) for H atoms.

† Lists of structure factors, anisotropic thermal parameters least-squares-planes equations and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53432 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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