Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and details of synthesis and a packing diagram have been deposited with the IUCr (Reference: BK1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). C**51**, 195–196

# (Tetraphenylporphyrinato)zirconium(IV) Diacetate

JEAN L. HUHMANN, JOYCE Y. COREY AND NIGAM P. RATH

*Department of Chemistry, University of Missouri–St Louis, St Louis, Missouri 63121, USA*

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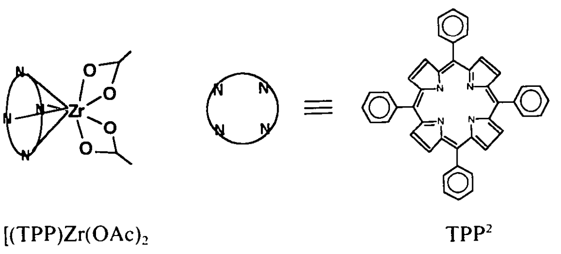
## Abstract

The title compound, bis(acetato-*O*,*O*′)[5,10,15,20-tetraphenyl-21*H*,23*H*-porphinato(2−)-$N^{21}$,$N^{22}$,$N^{23}$,$N^{24}$]zirconium, $[Zr(C_2H_3O_2)_2(C_{44}H_{28}N_4)].CH_2Cl_2$, crystallizes in space group $C2/c$ with $Z = 4$. The two acetate ligands are coordinated in a mutually *cis* configuration and the geometry about the Zr center approximates a square antiprism. The distance of the Zr atom from the porphyrin plane is 1.036 (7) Å. The average Zn—N and Zr—O bond distances are 2.257 (7) and 2.260 (6) Å, respectively, and the average $C_{carbonyl}$—Zr—$C_{carbonyl}$ and N—Zr—N($-x$, $y$, $\frac{1}{2}-z$) angles are 85.1 (4) and 125.4 (3)°, respectively.

## Comment

The title compound, $[(TPP)Zr(OAc)_2]$, was prepared by the reaction of (5,10,15,20-tetraphenylporphyrinato)zirconium(IV) dichloride with a refluxing mixture of acetic acid and pyridine (1:1.5), and crystallized by the addition of boiling $H_2O$. The diacetate was recrystallized from $CH_2Cl_2$–heptane solution (1:1) as the $CH_2Cl_2$ solvate. This procedure is similar to that described for the preparation of (2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) diacetate $[(OEP)Zr(OAc)_2]$ (Buchler *et al.*, 1971), the structure of which has been briefly mentioned and shows the metal to be eight-coordinate with bidentate *cis* acetate ligands (Hoard, 1975).



$[(TPP)Zr(OAc)_2]$ $TPP^2$

Related compounds which have been crystallographically characterized are $[(OEP)Zr(CH_2SiMe_3)_2]$ (Brand & Arnold, 1992), $[(TPP)ZrCl_2(thf)]$ (Kim, Whang, Kim & Do, 1993), $[(OEP)ZrCl_2]$, $[(OEP)Zr(O^tBu)_2]$ and $[(OEP)ZrMe_2].CH_2Cl_2$ (Brand & Arnold, 1993).

Group IV $d^0$ metalloporphyrins with *cis* coordination of ligands are of interest because of the potential analogy to Group IV $d^0$ metallocenes, the Ziegler–Natta catalysts that promote polymerization of ethylenes and propylene.

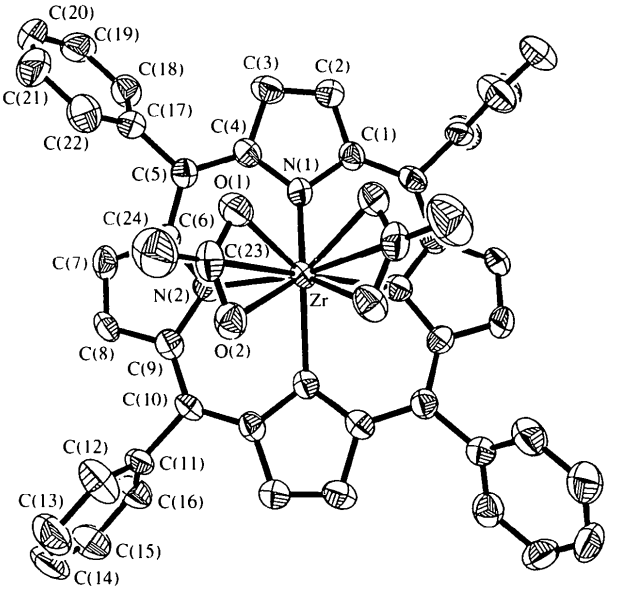


Fig. 1. Displacement ellipsoid drawing (*SHELXTL-Plus*; Sheldrick, 1991) of the title molecule. Ellipsoids enclose 50% probability and H atoms have been omitted. The molecule has twofold rotational symmetry.

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## Experimental

### *Crystal data*

$[Zr(C_2H_3O_2)_2(C_{44}H_{28}N_4)].$-$CH_2Cl_2$
$M_r = 906.9$
Monoclinic
$C2/c$
$a = 17.985$ (7) Å
$b = 15.900$ (7) Å
$c = 15.042$ (5) Å
$\beta = 104.23$ (4)°
$V = 4172$ (2) Å$^3$
$Z = 4$
$D_x = 1.444$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$13.5°$
$\mu = 0.443$ mm$^{-1}$
$T = 298$ K
Needle
0.5 × 0.1 × 0.1 mm
Purple

### *Data collection*

Siemens *R3m/V* diffractometer
$\theta$–$2\theta$ scans
Absorption correction: empirical ($\psi$ scan)
$T_{\min} = 0.648$, $T_{\max} = 0.681$
6492 measured reflections
3689 independent reflections
2191 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.0292$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 21$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 50 reflections
intensity decay: <4%

### *Refinement*

Refinement on $F$
$R = 0.0763$
$wR = 0.0822$
$S = 1.07$
3689 reflections
269 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0022F^2]$
$(\Delta/\sigma)_{\max} = 0.2$
$\Delta\rho_{\max} = 0.69$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.72$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Zr | 0 | 0.3101 (1) | 1/4 | 0.029 (1) |
| O(1) | 0.0411 (3) | 0.2111 (3) | 0.1671 (4) | 0.047 (2) |
| O(2) | 0.1035 (3) | 0.2268 (4) | 0.3087 (4) | 0.046 (2) |
| N(1) | −0.0508 (4) | 0.3714 (4) | 0.1141 (4) | 0.035 (2) |
| N(2) | 0.1007 (4) | 0.3792 (4) | 0.2181 (4) | 0.035 (2) |
| C(1) | −0.1293 (5) | 0.3822 (5) | 0.0764 (5) | 0.035 (3) |
| C(2) | −0.1421 (5) | 0.3808 (6) | −0.0215 (6) | 0.045 (3) |
| C(3) | −0.0757 (5) | 0.3704 (5) | −0.0444 (6) | 0.046 (3) |
| C(4) | −0.0169 (5) | 0.3675 (5) | 0.0415 (5) | 0.036 (3) |
| C(5) | 0.0613 (5) | 0.3692 (5) | 0.0487 (5) | 0.036 (3) |
| C(6) | 0.1160 (5) | 0.3827 (5) | 0.1332 (5) | 0.037 (3) |
| C(7) | 0.1942 (5) | 0.4045 (6) | 0.1414 (6) | 0.046 (4) |
| C(8) | 0.2276 (5) | 0.4136 (6) | 0.2306 (6) | 0.042 (3) |
| C(9) | 0.1705 (5) | 0.3961 (5) | 0.2803 (5) | 0.038 (3) |
| C(10) | 0.1835 (5) | 0.3965 (5) | 0.3736 (5) | 0.035 (3) |
| C(11) | 0.2646 (5) | 0.4135 (6) | 0.4293 (5) | 0.040 (3) |
| C(12) | 0.3148 (6) | 0.3480 (7) | 0.4533 (7) | 0.068 (4) |
| C(13) | 0.3895 (5) | 0.3655 (9) | 0.5047 (8) | 0.075 (5) |
| C(14) | 0.4113 (6) | 0.4428 (10) | 0.5317 (7) | 0.081 (5) |
| C(15) | 0.3611 (6) | 0.5094 (8) | 0.5083 (7) | 0.071 (5) |
| C(16) | 0.2876 (5) | 0.4935 (7) | 0.4559 (6) | 0.057 (4) |
| C(17) | 0.0913 (5) | 0.3579 (6) | −0.0349 (6) | 0.041 (3) |
| C(18) | 0.0741 (5) | 0.4135 (6) | −0.1077 (6) | 0.048 (4) |
| C(19) | 0.1021 (6) | 0.4009 (7) | −0.1849 (6) | 0.057 (4) |
| C(20) | 0.1472 (6) | 0.3331 (9) | −0.1892 (7) | 0.071 (5) |
| C(21) | 0.1659 (6) | 0.2778 (8) | −0.1170 (8) | 0.075 (5) |
| C(22) | 0.1382 (5) | 0.2898 (6) | −0.0401 (7) | 0.062 (4) |
| C(23) | 0.0952 (5) | 0.1877 (6) | 0.2344 (7) | 0.048 (3) |
| C(24) | 0.1471 (6) | 0.1173 (7) | 0.2272 (8) | 0.085 (5) |
| C(25) | 0 | 0.8234 (19) | 1/4 | 0.175 (11) |
| Cl | 0.0478 (8) | 0.9169 (10) | 0.2176 (10) | 0.224 (6) |
| Cl′ | 0.0433 (6) | 0.8531 (8) | 0.1762 (7) | 0.161 (4) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Zr—O(1) | 2.243 (6) | C(7)—C(8) | 1.337 (11) |
| Zr—N(1) | 2.246 (6) | C(9)—C(10) | 1.365 (11) |
| Zr—C(23) | 2.640 (10) | O(2)—C(23) | 1.254 (11) |
| Zr—O(2) | 2.278 (6) | N(1)—C(4) | 1.377 (12) |
| Zr—N(2) | 2.268 (7) | N(2)—C(9) | 1.395 (9) |
| O(1)—C(23) | 1.274 (10) | C(2)—C(3) | 1.330 (14) |
| N(1)—C(1) | 1.397 (10) | C(4)—C(5) | 1.385 (12) |
| N(2)—C(6) | 1.372 (11) | C(6)—C(7) | 1.424 (12) |
| C(1)—C(2) | 1.434 (12) | C(8)—C(9) | 1.438 (13) |
| C(3)—C(4) | 1.456 (11) | C(23)—C(24) | 1.480 (15) |
| C(5)—C(6) | 1.418 (10) | | |
| O(1)—Zr—O(2) | 57.2 (2) | O(1)—Zr—N(2) | 80.4 (2) |
| O(1)—Zr—O(2ⁱ) | 74.1 (2) | O(2ⁱ)—Zr—N(1) | 77.8 (2) |
| O(1)—Zr—O(1ⁱ) | 90.9 (3) | O(2)—Zr—N(2) | 75.2 (2) |
| O(2)—Zr—O(2ⁱ) | 108.9 (3) | N(2)—Zr—N(1ⁱ) | 79.3 (2) |
| N(1)—Zr—N(2) | 76.4 (2) | N(2)—Zr—N(2ⁱ) | 122.1 (3) |
| O(1)—Zr—N(1) | 85.1 (2) | C(23)—Zr—C(23ⁱ) | 85.1 (4) |

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The structure was solved by the Patterson method and refined successfully in the monoclinic space group *C2/c*. The crystal lattice contains a disordered molecule of $CH_2Cl_2$ which is positioned on a twofold rotation axis. The non-H atoms were refined anisotropically to convergence using full-matrix least-squares refinement by minimizing the function $w(F_o-F_c)^2$. All calculations were carried out using the *SHELXTL-Plus* (Sheldrick, 1991) structure determination package.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Tetraphenylphosphonium *cis*-Tetrabromobis(pyridine)molybdate(III)

Jurij V. Brenčič and Barbara Modec

*Department of Chemistry, University of Ljubljana, PO Box 537, Aškerčeva 5, 61001 Ljubljana, Slovenia*

Zhengui Yao

*Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA*

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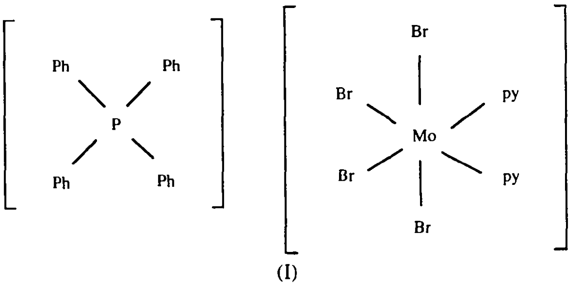
## Abstract

The title compound, $(C_{24}H_{20}P)[MoBr_4(C_5H_5N)_2]$, contains a *cis*-$[Mo^{III}Br_4(C_5H_5N)_2]^-$ anion in which Br and N atoms define a slightly distorted octahedron with average Mo—Br and Mo—N(pyridine) distances of 2.580 (5) and 2.220 (5) Å, respectively.

## Comment

Several salts of the $[MoBr_4py_2]^-$ anion (where py is pyridine) with univalent cations have been prepared recently (Brenčič, Leban & Modec, 1994). Because chemical and spectroscopic methods do not show unambiguously whether the pyridine ligands are *cis* or *trans*, crystal structure analysis remains the best method of identification.

In the title compound (I) (see Fig. 1, Tables 1 and 2), the pyridine ligands are found to be *cis* with respect to each other. Mo—Br and Mo—N(pyridine) distances are close to the respective values of 2.58 (1) and 2.22 (1) Å found in the crystal structure of the pyridinium salt of *trans*-$[MoBr_4py_2]^-$ (Brenčič, Čeh, Leban, Modec & Rotar, 1993). Each pyridine ring is rotated about its Mo—N bond so as to minimize contacts between the H atoms and the Br(1) and Br(2) atoms. The result of this is seen in the dissymmetry of the *cis*-$[MoBr_4py_2]^-$ anion. The unit cell contains two enantiomorphic pairs of anions. No information is available as to the possibility of separating the optical isomers.



(I)

Bond lengths and angles of the cation are comparable to those found for the crystal structure of $(PPh_4)[MoCl_4(bipy)]$ (Richards, Shortman, Povey & Smith, 1987).

The shortest contact between the anion and the cation is 3.622 (6) Å and occurs between atoms Br(2) and C(42)($x-1$, $\frac{3}{2}-y$, $\frac{1}{2}+z$).

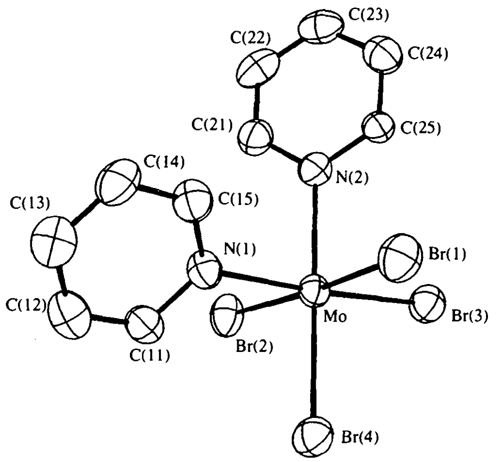


Fig. 1. The structure of the *cis*-$[MoBr_4py_2]^-$ anion with displacement ellipsoids drawn at the 50% probability level.

## Experimental

*Crystal data*

$(C_{24}H_{20}P)[MoBr_4(C_5H_5N)_2]$
$M_r = 913.18$
Monoclinic
$P2_1/c$
$a = 9.439$ (1) Å
$b = 21.600$ (3) Å
$c = 16.678$ (3) Å
$\beta = 94.71$ (1)°
$V = 3388.8$ (9) Å$^3$
$Z = 4$
$D_x = 1.79$ Mg m$^{-3}$
$D_m = 1.78$ (2) Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14$–16°
$\mu = 5.123$ mm$^{-1}$
$T = 293$ (1) K
Needle
0.48 × 0.22 × 0.18 mm
Red

*Data collection*

Nicolet *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ($\psi$ scan)
$T_{min} = 0.844$, $T_{max} = 0.999$
3592 measured reflections
3349 independent reflections
3221 observed reflections [$I \geq 3\sigma(I)$]

$R_{int} = 0.019$
$\theta_{max} = 23.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 24$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 500 min
intensity variation: none

*Refinement*

Refinement on *F*
$R = 0.0248$

$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.03$

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