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cis-Tetracarbonyldi(pyridine-*N*)tungsten(0), $[W(CO)_4(py)_2]$

JÜRGEN HOLZBOCK,[a] WOLFGANG SAWODNY,[a] ERIK GROSSE,[b] MICHAEL HASEIDL[b] AND LEONHARD WALZ[b]

[a]*Abteilung Anorganische Chemie, Universität Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany, and* [b]*Daimler-Benz AG, Forschungszentrum Ulm, F4N/P, Wilhelm-Runge-Strasse 11, D-89081 Ulm, Germany. E-mail: zf1wf48@newmat.dbag.ulm.daimlerbenz.com*

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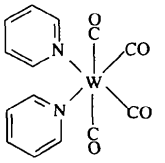
Abstract

In the title compound, $[W(C_5H_5N)_2(CO)_4]$, the W atom, on a crystallographic twofold rotation axis, is coordinated in a distorted octahedral geometry by four carbonyl ligands [W(1)—C(1) 1.956 (3) and W(1)—C(2) 2.027 (3) Å] and two pyridine ligands [W(1)—N(1) 2.272 (2) Å]. The molecules are packed in layers parallel to (001).

Comment

cis-Tetracarbonyldipyridinetungsten(0), (I), was prepared for the first time by reaction of hexacarbonyltungsten(0) with pyridine at 483 K in a sealed tube (Hieber & Romberg, 1935). According to dipole measurements, a structure with the pyridine ligands in a *cis* arrangement was proposed (Strohmeier & Langhäuser, 1961). The structure is now confirmed by X-ray analysis.



(I)

The molecular structure of (I) is shown in Fig. 1. The W atom is coordinated in a distorted octahedral geometry by two pyridine and four carbonyl ligands, with only moderate deviations from ideal 90 and 180° angles. The pyridine ligands are in *cis* positions and tilted by 42.3 (2)° with respect to the O(2)···O(2^i) axis, minimizing the contact of the H(3) and H(7) atoms with these carbonyl groups while avoiding mutual repulsion of the pyridine ligands [symmetry code: (i) $-x, y, \frac{1}{2}-z$]. The W—N distances [2.272 (2) Å], W—C distances (mean 1.99 Å) and the distances within the ligands show no anomalies, with the shorter W—C distance *trans* to pyridine.

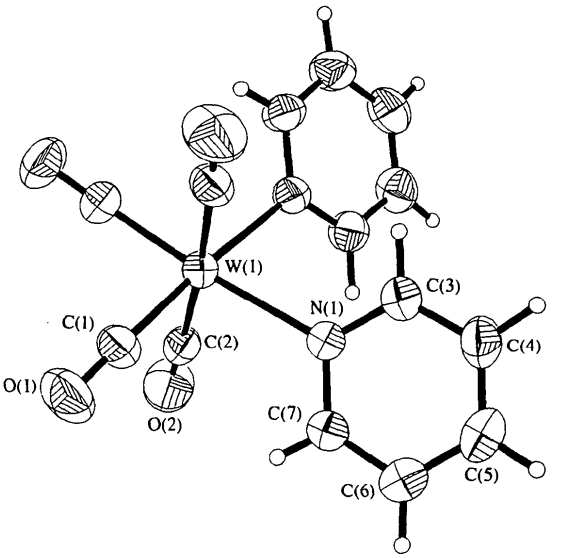


Fig. 1. The molecular structure of $[W(CO)_4(py)_2]$ with 50% probability ellipsoids.

The molecules are arranged in layers parallel to (001). Within each layer, all molecules are oriented with their two pyridine rings in the same direction relative to the *y* axis, with successive layers alternating in their orientation along $\pm y$. There are no particularly short intermolecular contacts.

Experimental

$[W(CO)_4(py)_2]$ was obtained from a solution of 5 g $[W(CO)_3(py)_3]$ (Hieber & Romberg, 1935) in 40 ml pyridine and 5 ml hydrofluoric acid by addition of 1.2 g solid dibenzoyl peroxide. The mixture was heated to 313 K for 10 min. A yellow product was then isolated by pouring the brown solution over ice. The precipitate was filtered off and washed several times with water. Yellow plate-like single crystals (raw yield 3.6 g) were grown from a mixture of acetone and hydrofluoric acid (40%) (ratio 90:10). Satisfactory analyses were obtained (C, H, N, W).

Crystal data

$[W(C_5H_5N)_2(CO)_4]$
M_r = 454.09
Monoclinic
$C2/c$
a = 7.430 (1) Å
b = 14.676 (2) Å
c = 13.406 (2) Å
β = 91.06 (1)°
V = 1461.6 (4) Å^3
Z = 4
D_x = 2.064 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from powder data (Cu $K\alpha$); 40 reflections
θ = 6–24°
μ = 7.919 mm^{-1}
T = 293 (2) K
Plate
0.70 × 0.31 × 0.09 mm
Yellow

Data collection

Stoe-modified Philips PW1100 diffractometer

1962 observed reflections [$I > 2\sigma(I)$]

$\theta/2\theta$ scans
Absorption correction: analytical
T_{min} = 0.112, T_{max} = 0.493
4279 measured reflections
2140 independent reflections

R_{int} = 0.0288
θ_{max} = 30.02°
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 100 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.0185
$wR(F^2)$ = 0.0456
S = 1.009
2140 reflections
117 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2 + 0.0625P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.003$

$\Delta\rho_{max}$ = 0.987 e Å^{-3}
$\Delta\rho_{min}$ = −1.162 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00042 (13)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
W(1)	0	0.632666 (9)	1/4	0.03584 (6)
C(1)	0.1416 (4)	0.5367 (2)	0.3155 (2)	0.0477 (6)
O(1)	0.2271 (4)	0.4796 (2)	0.3528 (2)	0.0715 (7)
C(2)	0.1793 (4)	0.6283 (2)	0.1380 (2)	0.0462 (6)
O(2)	0.2802 (5)	0.6216 (2)	0.0753 (2)	0.0781 (9)
N(1)	0.1453 (3)	0.7483 (2)	0.33031 (14)	0.0401 (4)
C(3)	0.0591 (4)	0.8212 (2)	0.3655 (2)	0.0494 (6)
C(4)	0.1455 (5)	0.8915 (3)	0.4159 (2)	0.0572 (7)
C(5)	0.3277 (5)	0.8875 (3)	0.4300 (2)	0.0580 (7)
C(6)	0.4186 (5)	0.8126 (3)	0.3957 (3)	0.0610 (8)
C(7)	0.3248 (4)	0.7449 (2)	0.3467 (2)	0.0507 (6)

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

W(1)—C(1)	1.956 (3)	C(1)—O(1)	1.160 (3)
W(1)—C(2)	2.027 (3)	C(2)—O(2)	1.140 (4)
W(1)—N(1)	2.272 (2)		
C(1^i)—W(1)—C(1)	87.90 (12)	C(2)—W(1)—N(1)	93.55 (9)
C(1^i)—W(1)—C(2)	89.99 (11)	C(2^i)—W(1)—N(1)	89.19 (10)
C(1)—W(1)—C(2)	87.37 (12)	N(1)—W(1)—N(1^i)	83.33 (11)
C(2)—W(1)—C(2^i)	176.34 (15)	O(1)—C(1)—W(1)	178.8 (2)
C(1^i)—W(1)—N(1)	175.80 (9)	O(2)—C(2)—W(1)	176.9 (3)
C(1)—W(1)—N(1)	94.47 (11)		

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

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nitrato(2,3,7,8,12,13,17,18-octaethylporphyrinato)iron(III)

MARY K. ELLISON, MAOYU SHANG, JUCHANG KIM AND W. ROBERT SCHEIDT

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: scheidt.1@nd.edu

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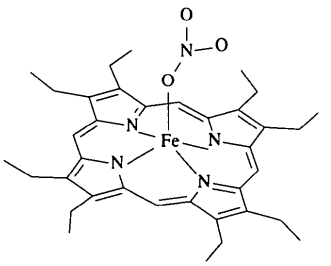
Abstract

The crystal structure of $[Fe(C_{36}H_{44}N_4)(NO_3)]$ has been determined in the space group $P\bar{1}$. The unit cell contains two molecules. The Fe atom is displaced out of the porphyrin plane by 0.50 Å, the average Fe—N_p distance is 2.056 (1) Å (where N_p is a porphyrin N atom) and the Fe—$O(NO_3)$ bond length is 2.016 (3) Å.

Comment

The isolation of the title five-coordinate iron(III)–nitrate complex, (I), resulted from attempts to isolate the six-coordinate iron(III)–nitro–nitrosyl species $[Fe(OEP)(NO)(NO_2)]$ (where OEP is 2,3,7,8,12,13,17,18-octaethylporphyrinato; Yoshimura, 1984; Settin & Fanning, 1988).



(I)

The average Fe—N_p bond length (where N_p is a porphyrin N atom) and the Fe—$O(NO_3)$ bond length are typical of high-spin iron(III)–porphyrin species (Scheidt & Reed, 1981) (Fig. 1). Average bond parameters and