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Nitro(*α*,*β*,*γ*,*δ*-tetraphenylporphyrinato)cobalt(III) benzene solvate

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.007 Å
R factor = 0.057
wR factor = 0.175
Data-to-parameter ratio = 9.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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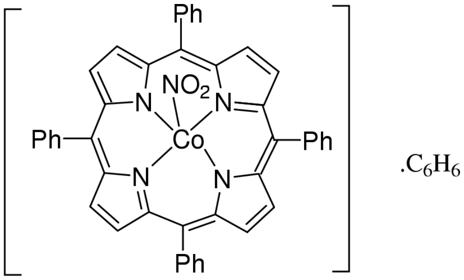
In the crystal structure of the title compound, $[Co(C_{44}H_{28}N_4)(NO_2)]\cdot C_6H_6$, the Co^{III} atom has a distorted square–pyramidal coordination, with the nitro ligand at the apical position. The Co—N(nitro) bond distance is 1.880 (3) Å.

Comment

The nitro-to-nitrito photo-isomerization of the title complex, $[Co(tpp)(NO_2)]$, where tpp is $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinate, was investigated in a benzene solution, using the laser flash technique (Seki *et al.*, 1997). The crystals, grown from a dimethylformamide (DMF) solution, were determined to be $[Co(tpp)(NO_2)(H_2O)]\cdot 2DMF$ and there was orientational disorder such that the positions of the nitro and aqua ligands were exchanged (Ohba *et al.*, 2000). The present paper reports the structure of the title compound, $[Co(tpp)(NO_2)]\cdot$benzene, (I), which was obtained from a benzene solution.



(I)

The Co atom has a distorted square–pyramidal coordination, with the nitro ligand at the apical position (Fig. 1). The Co atom is shifted by 0.147 (2) Å from the N5/N6/N7/N8 coordination plane towards the nitro ligand. In the tpp coordination plane, the N6—Co1—N8 linkage is almost linear, 177.5 (1)°, with both Co—N bond distances equal to 1.949 (3) Å (Table 1). On the other hand, the N5—Co1—N7 linkage is rather bent, 165.4 (1)°, and the Co—N distances, 1.962 (3)–1.963 (3) Å, are longer than in the linear N6—Co1—N8 linkage. The pyrrole ring moieties involving atoms N5 and N7 are bent away from the nitro group, and those involving atoms N6 and N8 are bent towards the nitro group. The dihedral angles between the N5/N6/N7/N8 plane and the pyrrole rings are 10.3 (1), 11.5 (1), 8.8 (1), and 12.4 (1)° for the N5, N6, N7, and N8 pyrrole rings, respectively.

The Co1—N4(nitro) bond length is 1.880 (3) Å. In the direction *trans* to the nitro group, there are van der Waals contacts between Co1 and atoms C10/C11 of a neighboring complex, with Co···C distances of 3.527 (4)–3.582 (4) Å,

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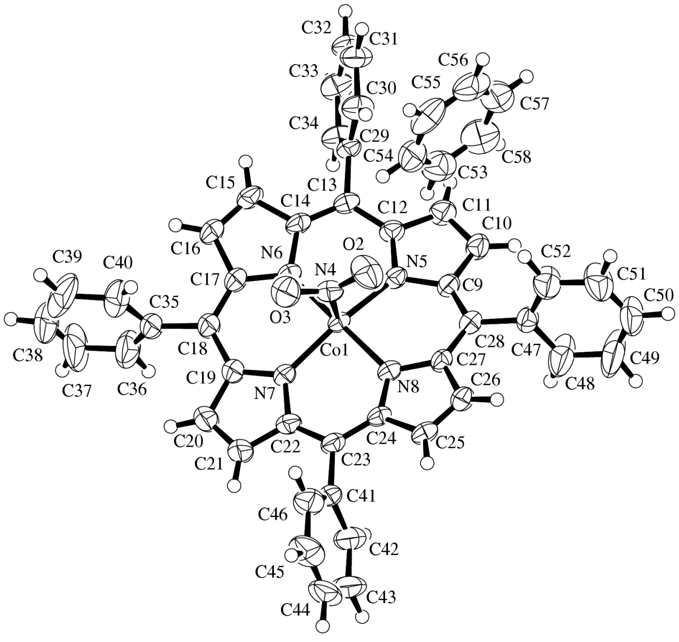

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. The disordered atoms C36*–C40* have been omitted for clarity.

forming a weakly connected centrosymmetric dimer in the crystal (Table 2 and Fig. 2).

Experimental

The preparation of the title complex has been described previously (Seki *et al.*, 1997). Crystals were grown from a benzene solution.

Crystal data

$[Co(C_{44}H_{28}N_4)(NO_2)]\cdot C_6H_6$
$M_r = 795.78$
Triclinic, $P\overline{1}$
$a = 12.352$ (2) Å
$b = 13.616$ (5) Å
$c = 12.118$ (3) Å
$\alpha = 102.47$ (2)°
$\beta = 102.31$ (2)°
$\gamma = 85.59$ (2)°
$V = 1943.2$ (9) Å^3

$Z = 2$
$D_x = 1.360$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 11.1$–$12.4°$
$\mu = 0.49$ mm^{-1}
$T = 297$ K
Prism, dark red
0.50 × 0.50 × 0.35 mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{min} = 0.782$, $T_{max} = 0.858$
7652 measured reflections
7257 independent reflections
7257 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$
$\theta_{max} = 26.5°$
$h = -15 \rightarrow 15$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: 21%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.175$
$S = 1.07$
7257 reflections
559 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0936P)^2 + 2.0291P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.89$ e Å^{-3}

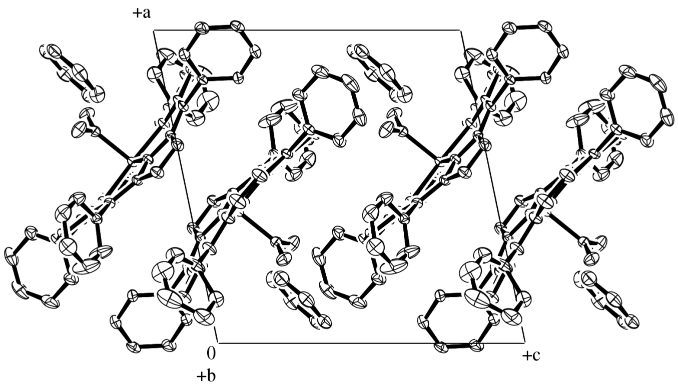

Figure 2
Projection of the crystal structure of (I) along *b*.

Table 1
Selected geometric parameters (Å, °).

Co1—N4	1.880 (3)	Co1—N8	1.949 (3)
Co1—N5	1.962 (3)	O2—N4	1.211 (5)
Co1—N6	1.949 (3)	O3—N4	1.225 (4)
Co1—N7	1.963 (3)		
N4—Co1—N5	97.9 (1)	N5—Co1—N8	90.2 (1)
N4—Co1—N6	91.1 (1)	N6—Co1—N7	90.5 (1)
N4—Co1—N7	96.7 (1)	N6—Co1—N8	177.5 (1)
N4—Co1—N8	91.3 (1)	N7—Co1—N8	89.6 (1)
N5—Co1—N6	89.2 (1)	O2—N4—O3	123.3 (4)
N5—Co1—N7	165.4 (1)		

Table 2
Contact distances (Å).

Co1···C11^i	3.527 (4)	Co1···C10^i	3.582 (4)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

The crystal specimen was sealed in a capillary with the mother liquor to avoid efflorescence. However, the intensity of the standard reflections decayed 21%, for which a correction was applied. As a result of movement of the crystal in the capillary, data collection was interrupted in the 2θ shell 50–53°. The completeness of the data collection was 0.90 for $2\theta_{max} = 53°$. One of the phenyl groups of tpp shows orientational disorder. Atoms C36*, C37*, C39* and C40* were introduced for a second orientation with 50% probability. The dihedral angle between the two orientations of the ring is 40.2 (5)°. All H-atom positional parameters were calculated geometrically, and fixed with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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