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Aquanitro($\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinato)cobalt(III) *N,N*-dimethylformamide disolvate

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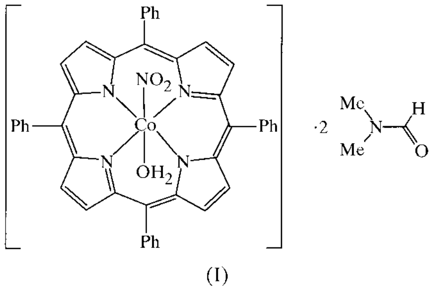
In the title compound, [Co(tpp)(NO$_2$)(H$_2$O)]·2dmf or [Co(C$_{44}$H$_{28}$N$_4$)(NO$_2$)(H$_2$O)]·2C$_3$H$_7$NO, a distorted octahedral Co^{III} complex shows an orientational disorder such that the positions of the nitro and aqua ligands are exchanged. As a result, the averaged structure has an inversion centre at the Co atom. The dimethylformamide molecule also has a positional disorder.

Comment

The nitro-to-nitrito photoisomerization of the title complex, [Co(tpp)(NO$_2$)(H$_2$O)], (I), where tpp is $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinate, was investigated in benzene solution using a laser flash technique. The thermodynamically less stable nitrito form was detected and the nitrito-to-nitro back reaction obeyed first-order kinetics with a rate constant $k_1 = 3.0 \times 10^2$ s^{-1} (Seki *et al.*, 1997). The half-life ($t_{1/2}$) was calculated to be 2.3 ms, which is much shorter than that of [Co(NH$_3$)$_5$(ONO)]$^{2+}$ in aqueous solution ($k_1 = 0.76 \times 10^{-4}$ s^{-1} and $t_{1/2}$ = 2.5 h; Miyoshi *et al.*, 1983).



(I)

The dimethylformamide (dmf) molecule exists near the axial ligands, and has two possible orientations with 50% probability each. In one of them (atoms O5, N10 and C34–C36), dmf seems to form a hydrogen bond with the aqua O4 atom, with an O5···O4^{i} distance of 2.754 (4) Å [symmetry code: (i) $-x, -y, -z$]. In the other orientation, dmf (atoms O6, N11 and C37–C39) is close to the nitro ligand, with an O2···C39 distance of 3.30 (2) Å.

Experimental

The preparation of the title complex has been described previously (Seki *et al.*, 1997). Crystals of (I) were grown from a dmf solution. The crystal specimen was sealed in a capillary with the mother liquor to avoid efflorescence.

Crystal data

[Co(C$_{44}$H$_{28}$N$_4$)(H$_2$O)-(NO$_2$)]·2C$_3$H$_7$NO
M_r = 881.87
Triclinic, $P\overline{1}$
a = 10.355 (1) Å
b = 11.815 (2) Å
c = 9.900 (1) Å
α = 105.06 (1)°
β = 97.47 (1)°
γ = 107.58 (1)°
V = 1086.0 (3) Å^3
Z = 1
D_x = 1.348 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 13.7–15.0°
μ = 0.453 mm^{-1}
T = 298 (1) K
Prismatic, violet
0.60 × 0.20 × 0.15 mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\rm min}$ = 0.900, $T_{\rm max}$ = 0.928
5271 measured reflections
4996 independent reflections
3676 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 27.5°
$h = 0 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.043
$wR(F^2)$ = 0.123
S = 1.01
4996 reflections
340 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.3931P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O4	1.962 (2)	Co1—N9	1.981 (2)
Co1—N7	1.962 (2)	N7—O2	1.214 (4)
Co1—N8	1.983 (2)	N7—O3	1.255 (6)
O2—N7—O3	115.8 (3)		

The Co^{III}—OH$_2$ bond distances in other Co(tpp) complexes are in the range 1.932 (8)–1.979 (3) Å (Masuda *et al.*, 1982; Iimura *et al.*, 1988), and Co^{III}—NO$_2$ distances are in the range 1.897 (11)–1.948 (4) Å (Kaduk & Scheidt, 1974; Yamamoto & Iitaka, 1989). Therefore, a split-site model was not applicable for positional disorder of the nitro N7 and aqua O4 atoms. It was assumed that the N7 and O4 atoms share the same positional and atomic displacement parameters. The dmf molecule exists near the axial ligands, showing positional disorder. Two possible positions having different orientations were assumed with 50% probability each. The H atoms of the aqua ligand were not introduced because they were not located from difference syntheses. The other H-atom positional parameters were calculated geometrically and fixed (C—H = 0.95 Å) with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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