Data collection

Siemens SMART area detector diffractometer
ω rotation with narrow frame scans
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.019$, $T_{\max} = 0.064$
7156 measured reflections
2606 independent reflections
2134 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 27.46°$
$h = -10 \rightarrow 9$
$k = -16 \rightarrow 15$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.057$
$S = 0.818$
2606 reflections
82 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 3.591P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sb1—I2	2.7574 (5)	Sb1—O1^{i}	2.854 (4)
Sb1—I1	2.7610 (5)	Sb1—O1	3.020 (4)
Sb1—I3	2.7974 (5)	Sb1—I3^{ii}	3.6842 (5)
I2—Sb1—I1	94.64 (2)	I3—Sb1—O1	84.37 (8)
I2—Sb1—I3	93.49 (2)	O1^{i}—Sb1—O1	95.22 (11)
I1—Sb1—I3	96.65 (2)	I2—Sb1—I3^{ii}	174.02 (2)
I2—Sb1—O1^{i}	82.66 (8)	I1—Sb1—I3^{ii}	83.385 (14)
I1—Sb1—O1^{i}	83.58 (8)	I3—Sb1—I3^{ii}	81.156 (14)
I3—Sb1—O1^{i}	176.15 (8)	O1^{i}—Sb1—I3^{ii}	102.68 (8)
I2—Sb1—O1	82.45 (8)	O1—Sb1—I3^{ii}	99.58 (7)
I1—Sb1—O1	176.99 (8)		

Symmetry codes: (i) $-x, 2-y, 2-z$; (ii) $1-x, 2-y, 2-z$.

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 30 s exposure for (1) and 20 s for (2). A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 88 and 180° with the area detector held at $2\theta = -27°$. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the $U_{\rm iso}$ value of their attached C atom for aromatics and 1.5 times $U_{\rm iso}$ for all others.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1150). Services for accessing these data are described at the back of the journal.

References

Carmalt, C. J., Clegg, W., Elsegood, M. R. J., Errington, R. J., Havelock, J., Lightfoot, P., Norman, N. C. & Scott, A. J. (1996). *Inorg. Chem.* **35**, 3709–3712.

Eveland, J. R. & Whitmire, K. H. (1996). *Inorg. Chim. Acta*, **249**, 41–46.

Herzog, A., Feng-Quan, L., Roesky, H. W., Demsar, A., Keller, K., Noltemeyer, M. & Pauer, F. (1994). *Organometallics*, **13**, 1251–1256.

Krautscheid, V. H. (1994*a*). *Z. Anorg. Allg. Chem.* **620**, 1559–1564.

Krautscheid, V. H. (1994*b*). Personal communication.

Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SADABS. Program for Absorption Correction*. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sigwarth, B., Weber, U., Zsolnai, L. & Huttner, G. (1985). *Chem. Ber.* **118**, 3114–3126.

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Bis(pyridine-*N*)(7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrinato)nickel(II) Dimethanol Solvate

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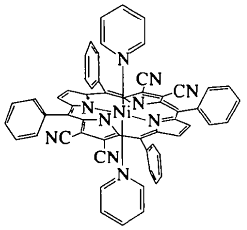
Abstract

The title compound, $[\mathrm{Ni(C_{48}H_{24}N_8)(C_5H_5N)_2}].2\mathrm{CH_4O}$, is a high-spin bis(pyridine)–Ni$^{\rm II}$ derivative of an antipodally β-pyrrole–tetracyano-substituted *meso*-tetraphenylporphyrin. The $[\mathrm{Ni(py)_2\{tpp(CN)_4\}}]$ molecule [py is pyridine and $\mathrm{tpp(CN)_4}$ is 7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrinato] lies on a crystallographic centre of symmetry, but its non-crystallographic symmetry is close to D_{2h}. The core of the $\mathrm{tpp(CN)_4}$ porphyrin dianion is essentially planar. The high-spin state of the Ni$^{\rm II}$ cation leads to a lengthening of the Ni—N(pyrrole) bond distances relative to those present in the low-spin [Ni$^{\rm II}$tpp] derivative. Moreover, the electron-withdrawing β-pyrrole cyano substituents, which lie in the antipodal pyrrolic rings, cause an increase in the C7—C8 and the antipodal C7′—C8′ bond distances as well as an opening of the C6—N2—C9 and the antipodal C6′—N2′—C9′ bond angles.

Comment

During the course of our studies concerning the conformations and properties of β-pyrrole-substituted *meso*-tetraarylporphyrins (Ochsenbein *et al.*, 1994), we have isolated the title compound, (I), in which the Ni^{II} cation is six-coordinated and high-spin ($S = 1$). The regioselective substitution of the four β-pyrrole H atoms of the tetraphenylporphyrin (H_2tpp) by four cyano substituents was achieved using the methods described by Callot (1974) and more recently by Crossley, Burn, Chew, Cuttance & Newsom (1991). The electron-withdrawing cyano substituents of $[tpp(CN)_4]^{2-}$ enhance the complexing power of the central Ni^{II} cation towards axial ligation, compared to the relative inertness of the non-substituted nickel(II) tetraphenylporphyrin, Ni(tpp). Indeed, addition of 1000 equivalents of pyridine at room temperature to a solution of $[Ni\{tpp(CN)_4\}]$ leads quantitatively to $[Ni\{tpp(CN)_4\}(py)_2]$, while pure $[Ni(tpp)(py)_2]$ can not be obtained at room temperature even with pyridine as the solvent. The spin-state changes of Ni^{II} from $S = 0$ in $[Ni\{tpp(CN)_4\}]$ to $S = 1$ in $[Ni\{tpp(CN)_4\}(py)_2]$ by addition of two pyridine axial ligands is indicated by ^1H NMR and UV–visible spectroscopy in dichloromethane/pyridine (10:1) solution. Giraudeau, Gross & Callot (1981) have already reported the axial ligation of pyridine to $[Ni\{tpp(CN)_4\}]$ but no attempts were made to isolate this derivative.



(I)

The title complex (Fig. 1) lies on a crystallographic centre of inversion and the Ni^{II} cation is hexacoordinated, as expected. The pyridine rings are perpendicular to the mean plane of the porphyrinato core (four N atoms and 20 C atoms) and the dihedral angle φ (Collins, Countryman & Hoard, 1972) between the plane of the pyridine ring and a plane defined by the N2, Ni and N5 positions is 27.7 (2)°. The porphyrin is essentially planar, with the largest deviations from the mean plane of the porphyrinato core being at the C7 and C10 atoms, which are displaced by 0.134 (3) and 0.117 (3) Å, respectively. The pyrrole rings are planar as usual (maximum deviation = 0.02 Å) and the deviations of the two independent cyano groups from the mean plane of the porphyrinato core are 0.398 (4) and 0.07 (3) Å for C11 and C12, respectively. The angles C7—C11—N3 and C8—C12—N4 are identical [173.6 (3)°].

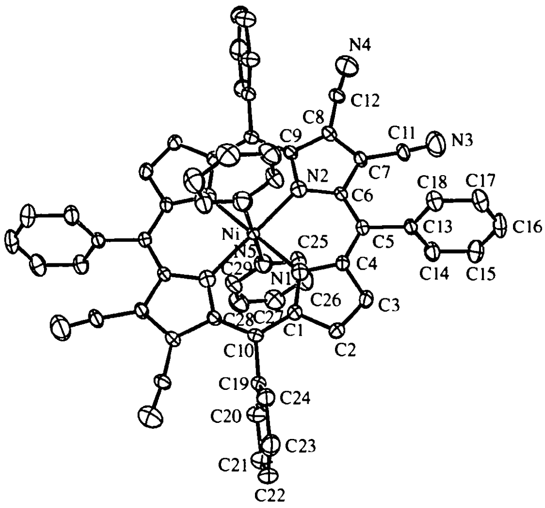


Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the $[Ni\{tpp(CN)_4\}(py)_2]$ molecule showing the atom-labelling scheme used. Displacement ellipsoids are drawn at the 50% probability level.

The molecular structure of $[Ni\{tpp(CN)_4\}(py)_2]$ is similar to that of the six-coordinated high-spin [5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrin]bis(imidazole)-nickel(II) derivative, $[Ni(ImH)_2\{t(4\text{-}Me\text{-}py)p\}]$, described by Kirner, Garofalo & Scheidt (1975). The independent axial Ni—N(pyridine) bond length is 2.240 (2) Å in $[Ni\{tpp(CN)_4\}(py)_2]$. The two independent equatorial Ni—N(pyrrole) bond distances differ significantly. Two short Ni—N(pyrrole) distances of 2.030 (2) Å occur with the N atoms N1 and N1′ belonging to the two antipodal non-substituted pyrrole rings. This bond distance is comparable to the Ni—N(pyrrole) distance of 2.038 (2) Å observed in $[Ni(ImH)_2\{t(4\text{-}Me\text{-}py)p\}]$. Two long Ni—N(pyrrole) bond lengths of 2.079 (2) Å occur with the two N atoms N2 and N2′ belonging to the pyrrole rings which are antipodally dicyanated. The Ni—N(pyrrole) bond distance of 2.030 (2) Å is already long, relative to the mean Ni—N(pyrrole) bond length of 1.928 (3) Å present in the diamagnetic four-coordinate Ni^{II}(tpp) derivative (Smith, 1975). This lengthening is in agreement with the high-spin state of the Ni^{II} cation in $[Ni\{tpp(CN)_4\}(py)_2]$, having unpaired electrons in the d_{z^2} orbital as well as in the $d_{x^2-y^2}$ orbital, these electrons being both antibonding with respect to the lone pairs of the pyridines and the pyrroles. The further lengthening of the Ni—N(pyrrole) bond distances, with the N atoms belonging to cyanated pyrrole rings [2.079 (2) Å], is due to the electron-withdrawing effect of the cyano groups. Thus, the symmetry of the Ni^{II} cation in $[Ni\{tpp(CN)_4\}(py)_2]$ is close to D_{2h}. Moreover, the C_β—C_β bond distances in the non-cyanated and cyanated pyrrole rings are 1.343 (3) and 1.374 (4) Å, respectively. As a result of the lengthening, by 0.03 Å, of the C_β—C_β bond distance in the cyanated pyrrole rings, the corresponding C_α—N(pyrrole)—C_α angles increase by approximately 2°.

Experimental

The title compound was prepared in quantitative yield by adding 1000 equivalents of pyridine to a 1.4 $\times 10^{-4}$ *M* solution of [Ni(tpp)(CN)$_4$] (Callot, 1974) in dichloromethane at room temperature. After evaporation of the solvent, the solid was washed with hexane and dried under vacuum, resulting in dark-blue crystalline material. Single crystals suitable for X-ray analysis were obtained by slow diffusion of methanol into a solution of [Ni(tpp)(CN)$_4$] in dichloromethane/pyridine (10:1). ^{1}H NMR (CDCl$_3$, δ, p.p.m.): 49.1 (broad, H_β), 9.1–7.5 (broad, H_{phenyl}). UV–visible (CH$_2$Cl$_2$, λ, nm): 446, 467 (Soret band), 695.

Crystal data

$[Ni(C_{48}H_{24}N_8)(C_5H_5N)_2].2CH_4O$
$M_r = 993.78$
Triclinic
$P\overline{1}$
$a = 9.349\,(2)$ Å
$b = 11.853\,(3)$ Å
$c = 13.548\,(4)$ Å
$\alpha = 77.92\,(2)^\circ$
$\beta = 69.70\,(2)^\circ$
$\gamma = 68.38\,(2)^\circ$
$V = 1303.3\,(6)$ Å^3
$Z = 1$
$D_x = 1.27$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18$–20°
$\mu = 0.423$ mm^{-1}
$T = 294$ K
Parallelepipedic
0.40 × 0.35 × 0.20 mm
Dark blue

Data collection

Enraf–Nonius MACH3 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.903$, $T_{max} = 0.919$
4808 measured reflections
4564 independent reflections

3797 reflections with $I > 3\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 25^\circ$
$h = -10 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 16$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.074$
$S = 1.651$
3797 reflections
331 parameters
H atoms included but not refined

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.08F_o^4]$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.111$ e Å^{-3}
$\Delta\rho_{min} = -0.120$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ni—N1	2.030 (2)	C7—C11	1.434 (3)
Ni—N2	2.079 (2)	C8—C12	1.428 (3)
Ni—N5	2.240 (2)	C11—N3	1.139 (3)
C2—C3	1.343 (3)	C12—N4	1.146 (3)
C7—C8	1.374 (4)		
C1—N1—C4	106.8 (2)	C7—C11—N3	173.6 (3)
C6—N2—C9	108.7 (2)	C8—C12—N4	173.6 (3)

No H atoms could be located for the methanol solvent.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1059). Services for accessing these data are described at the back of the journal.

References

Callot, H. J. (1974). *Bull. Soc. Chim. Fr.* pp. 1492–1495.
Collins, D. M., Countryman, R. & Hoard, J. L. (1972). *J. Am. Chem. Soc.* **94**, 2066–2071.
Crossley, M. J., Burn, P. L., Chew, S. S., Cuttance, F. B. & Newsom, I. A. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1564–1566.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Giraudeau, A., Gross, M. & Callot, H. J. (1981). *Electrochim. Acta*, **26**, 1839–1843.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kirner, J. F., Garofalo, J. & Scheidt, W. R. (1975). *Inorg. Nucl. Chem. Lett.* **11**, 107–112.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ochsenbein, P., Ayougou, K., Mandon, D., Fischer, J., Weiss, R., Austin, R. N., Jyaraj, K., Gold, A., Terner, J. & Fajer, J. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 348–350.
Smith, K. M. (1975). In *Porphyrins and Metalloporphyrins*. Amsterdam: Elsevier.

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Zinc(II) Acetate Dihydrate

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Abstract

The Zn atom in bis(acetato-*O*,*O*′)diaquazinc(II), [Zn(CH$_3$COO)$_2$(H$_2$O)$_2$], adopts a distorted octahedral structure coordinated by two water O atoms and four acetate O atoms.