Crystal structures of the methylene chloride disolvates of tetrakis(3,5-dimethoxyphenyl)porphyrin and its isotypic copper(II) and nickel(II) complexes, $C_{52}H_{46}N_4O_8 \cdot 2CH_2Cl_2$, $Cu(C_{52}H_{44}N_4O_8) \cdot 2CH_2Cl_2$, $Ni(C_{52}H_{44}N_4O_8) \cdot 2CH_2Cl_2$

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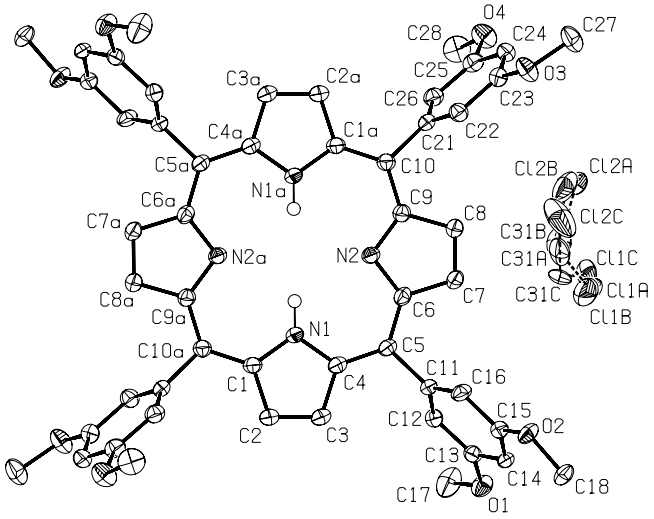

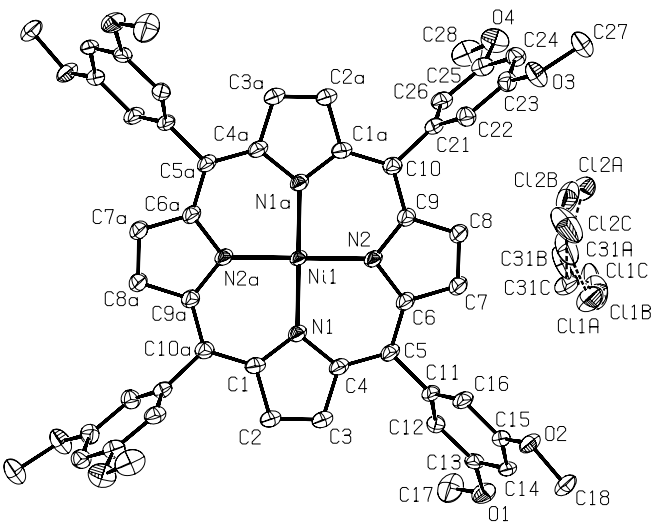

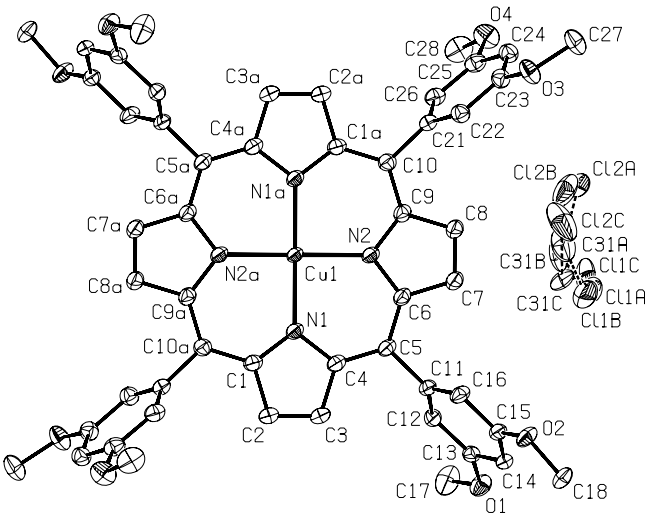

Abstract

$C_{54}H_{50}Cl_4N_4O_8$, triclinic, $P\bar{1}$ (no. 2), a = 11.295(1) Å, b = 11.255(1) Å, c = 11.797(1) Å, α = 108.904(2)°, β = 101.091(2)°, γ = 110.992(2)°, V = 1241.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.056, $wR_{ref}(F^2)$ = 0.135, T = 100 K.

$C_{54}H_{48}Cl_4CuN_4O_8$, triclinic, $P\bar{1}$ (no. 2), a = 11.2204(5) Å, b = 11.3499(6) Å, c = 11.7610(6) Å, α = 109.187(1)°, β = 100.830(1)°, γ = 110.681(1)°, V = 1242.7 Å^3, Z = 1, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.092, T = 100 K.

$C_{54}H_{48}Cl_4N_4NiO_8$, triclinic, $P\bar{1}$ (no. 2), a = 11.196(1) Å, b = 11.329(1) Å, c = 11.785(1) Å, α = 109.486(2)°, β = 101.230(2)°, γ = 110.607(2)°, V = 1233.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.110, T = 100 K.

Source of material

100 ml of propionic acid were heated to reflux (413 K). 2.4 g of 3,5-dimethoxybenzaldehyde were added, followed by dropwise addition of pyrrole (1 ml, 0.01443 mol). After the addition was completed, the mixture was stirred for an additional 0.5 h, allowed to cool to 240 K, and methanol (200 ml) was added dropwise. The solution was allowed to cool to room temperature and then stored for 3-4 h at 260 K (freezer) to form a purple crystalline solid (**I**). The crystals were collected by filtration and washed

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with methanol until the solution rinsed off colorless. The crystals were dried in vacuum to yield 0.64 g (27.8 %). The copper and nickel complexes **II** and **III**, respectively, were synthesized from **I** by reaction with Cu(II) or Ni(II) acetate in DMF at reflux temperature for 45 minutes. The products were precipitated with methanol, collected by filtration, and rinsed with methanol until the solutions were clear. Additional product precipitated from the washing solutions over night at 260 K in the freezer. The purple solids were dried in vacuum. All single crystals were grown by slow diffusion of hexane into a solution of **I**, **II**, or **III** in methylene chloride in small test tubes.

Experimental details

The crystals tend to desolvate in air at room temperature when taken out of solution. They were mounted on the goniometerhead with the help of a small drop of mineral oil and were immediately transferred into to the cold stream of the diffractometer.

For the purpose of the refinement a static disorder with three partially occupied and overlapping solvate molecules was assumed. The refined occupancy distributions for the three structures are similar but not quite identical (0.43(1), 0.36(2), and 0.176(4) for **I**, 0.48(1), 0.31(1) and 0.180(3) for **II**, and 0.483(9), 0.25(1) and 0.249(5) for **III**).

Discussion

The free base porphyrin (**I**), the copper complex (**II**), and the nickel derivative (**III**) were found to be isomorphous and are crystallizing with the center of the porphyrin located in a crystallographic inversion center. Isomorphism among related porphyrin complexes is not unusual and is often observed for the more rigid members of the porphyrin family. Exchange of the central metal as well as variation of the co-crystallizing solvates often results in conservation of the overall packing pattern and related compounds often form an isomorphous and/or isostructural series [2-4]. The unit cell parameters of compounds **I**, **II** and **III** are very similar. The unit cell volumes at 100 K are differing by less than 0.5 % from their average value and the largest variation for any of the unit cell axes, found for the *a* axis of the Cu complex (**II**), is 0.056 Å or 0.49 % of the median value. The three congeners are essentially isostructural and were refined with the same set of parameters and restraints, differing only by the presence of either a central Ni or Cu atom for the metal complexes or the pyrrole hydrogen atom for the free base porphyrin. All substituents as well as the disordered methylene chloride solvate molecules exhibit essentially the same orientation. The porphyrin moieties of all three molecules are basically planar. The r.m.s. deviations from the planes defined by C1 to C11, C21, N1, N2 and (for **II** and **III**) the metal atom are 0.0344 Å for **I**, 0.0249 Å for **II**, and 0.0273 Å for **III**. The largest deviation from planarity is 0.055(1) Å for C11 of the Ni complex (**III**). The 3,5-methoxy substituents are tilted with respect to the porphyrin moiety by about 71° for phenyl ring C11 to C16 and 77° for C21 to C26 (70.06(2)° and 77.00(4)°, respectively, for **I**, 71.57(1)° and 76.85(3)°, respectively, for **II** and 71.81(2)° and 77.70(3)°, respectively, for **III**). The methoxy units are basically in plane with the benzene ring, the largest deviation observed is 0.185(2) Å for C28 of Cu complex (**II**). The porphyrin planes of the molecules are approximately perpendicular to the $[1\bar{1}0]$ direction. They are in parallel to each other, but each molecule is offset by half a unit cell with respect to its next neighbor.

Due to the sterically demanding methoxy groups no π-π stacking interactions are observed. The packing seems to be guided by the spacial demands of the substituents and some weak interactions of the methoxy and phenyl hydrogen atoms with neighboring oxygen and nitrogen atoms. The most pronounced of these interactions are between H18C and O4^{i}, O18B and N2^{ii} and H16 and O2^{ii} (symmetry codes i: 1–*x*,–*y*,1–*z*; ii: 1–*x*,1–*y*,1–*z*) which are 2.498 Å, 2.597 Å, and 2.592 Å for **I**, 2.502 Å, 2.626 Å, and 2.571 Å for **II**, and 2.498 Å, 2.611 Å, 2.586 Å for **III**. For the two metal complexes additional close contacts between methoxy hydrogen atoms H27B^{iii} and H28B^{iv} and Cu1 or Ni1 are observed. The values are 3.248 Å and 3.169 Å for the copper compound (**II**), and 3.234 Å and 3.137 Å for the nickel complex (**III**) (symmetry codes iii: –1+*x*,*y*,*z*; iv: *x*,1+*y*,*z*). The remaining voids left between the porphyrin and methoxy benzene units are occupied by two disordered methylene chloride molecules. As evident by the large degree of thermal motion the solvate molecules are not large enough to entirely fill the remaining space, but they seem to be swaying back and forth along the Cl–C–Cl line.

1. Tetrakis(3,5-dimethoxyphenyl)porphyrin methylene chloride disolvate, $C_{52}H_{46}N_4O_8 \cdot 2CH_2Cl_2$

Table 1. Data collection and handling.

Crystal:	red plate, size 0.03 × 0.22 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.91 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12895, 6122
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5657
$N(param)_{refined}$:	377
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	2*i*		–0.0303	0.0791	0.0731	0.022
H(2)	2*i*		–0.1809	0.3484	0.1978	0.028
H(3)	2*i*		–0.0053	0.3822	0.3844	0.027
H(7)	2*i*		0.3205	0.1446	0.4487	0.026
H(8)	2*i*		0.3703	–0.0316	0.3027	0.026
H(12)	2*i*		0.0155	0.2056	0.5104	0.023
H(14)	2*i*		0.3357	0.5340	0.8175	0.021
H(16)	2*i*		0.3656	0.4176	0.4642	0.025
H(17A)	2*i*		–0.0911	0.2660	0.6505	0.060
H(17B)	2*i*		–0.0704	0.2543	0.7838	0.060
H(17C)	2*i*		–0.0393	0.1575	0.6724	0.060
H(18A)	2*i*		0.4950	0.7473	0.8348	0.035
H(18B)	2*i*		0.6442	0.7730	0.8364	0.035
H(18C)	2*i*		0.5591	0.6553	0.8761	0.035
H(22)	2*i*		0.4849	–0.0390	0.0888	0.025
H(24)	2*i*		0.5484	–0.3570	0.1339	0.026
H(26)	2*i*		0.1675	–0.3923	0.0401	0.026
H(27A)	2*i*		0.7608	–0.1578	0.2618	0.050
H(27B)	2*i*		0.8574	–0.0834	0.1968	0.050
H(27C)	2*i*		0.7441	–0.2437	0.1171	0.050
H(28A)	2*i*		0.1557	–0.5396	0.1474	0.051
H(28B)	2*i*		0.1635	–0.6849	0.0875	0.051
H(28C)	2*i*		0.1148	–0.6204	–0.0040	0.051
H(31A)	2*i*	0.43	0.5786	0.2372	0.3917	0.050
H(31B)	2*i*	0.43	0.7377	0.3334	0.4683	0.050
H(31C)	2*i*	0.36	0.5781	0.2716	0.4160	0.050
H(31D)	2*i*	0.36	0.7365	0.3617	0.4958	0.050
H(31E)	2*i*	0.176	0.5571	0.3160	0.4660	0.027
H(31F)	2*i*	0.176	0.7019	0.4118	0.5781	0.027

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		–0.1360(2)	0.1906(2)	0.0846(2)	0.0203(7)	0.0177(7)	0.0182(7)	0.0097(6)	0.0075(6)	0.0056(6)
C(2)	2*i*		–0.1284(2)	0.2985(2)	0.1959(2)	0.0277(8)	0.0238(8)	0.0181(7)	0.0157(7)	0.0075(6)	0.0050(6)
C(3)	2*i*		–0.0323(2)	0.3168(2)	0.2983(2)	0.0271(8)	0.0221(8)	0.0166(7)	0.0132(7)	0.0074(6)	0.0044(6)
C(4)	2*i*		0.0211(2)	0.2199(2)	0.2533(2)	0.0191(7)	0.0171(7)	0.0163(7)	0.0071(6)	0.0066(6)	0.0044(6)
C(5)	2*i*		0.1230(2)	0.2049(2)	0.3264(1)	0.0158(7)	0.0176(7)	0.0149(7)	0.0053(6)	0.0055(6)	0.0034(6)
C(6)	2*i*		0.1770(2)	0.1127(2)	0.2785(2)	0.0157(7)	0.0197(7)	0.0154(7)	0.0054(6)	0.0040(6)	0.0049(6)
C(7)	2*i*		0.2800(2)	0.0969(2)	0.3582(2)	0.0185(7)	0.0233(8)	0.0156(7)	0.0085(6)	0.0028(6)	0.0038(6)
C(8)	2*i*		0.3071(2)	0.0012(2)	0.2789(2)	0.0192(7)	0.0236(8)	0.0176(7)	0.0103(6)	0.0036(6)	0.0052(6)
C(9)	2*i*		0.2208(2)	–0.0420(2)	0.1498(2)	0.0164(7)	0.0181(7)	0.0182(7)	0.0069(6)	0.0050(6)	0.0055(6)
C(10)	2*i*		0.2196(2)	–0.1423(2)	0.0409(2)	0.0188(7)	0.0171(7)	0.0187(7)	0.0085(6)	0.0066(6)	0.0064(6)
C(11)	2*i*		0.1828(2)	0.2987(2)	0.4672(1)	0.0179(7)	0.0179(7)	0.0147(7)	0.0091(6)	0.0038(6)	0.0028(6)
C(12)	2*i*		0.1059(2)	0.2783(2)	0.5456(2)	0.0170(7)	0.0200(7)	0.0188(7)	0.0083(6)	0.0053(6)	0.0072(6)
C(13)	2*i*		0.1643(2)	0.3663(2)	0.6754(2)	0.0211(7)	0.0221(7)	0.0183(7)	0.0132(6)	0.0089(6)	0.0101(6)
C(14)	2*i*		0.2967(2)	0.4747(2)	0.7284(1)	0.0228(7)	0.0166(7)	0.0124(6)	0.0108(6)	0.0045(6)	0.0040(5)
C(15)	2*i*		0.3703(2)	0.4943(2)	0.6490(2)	0.0185(7)	0.0179(7)	0.0185(7)	0.0086(6)	0.0048(6)	0.0051(6)
C(16)	2*i*		0.3140(2)	0.4051(2)	0.5179(2)	0.0204(7)	0.0225(8)	0.0164(7)	0.0086(6)	0.0089(6)	0.0038(6)
C(17)	2*i*		–0.0357(2)	0.2503(3)	0.7134(2)	0.0256(9)	0.057(1)	0.028(1)	0.0074(9)	0.0139(8)	0.0165(9)
C(18)	2*i*		0.5535(2)	0.7018(2)	0.8193(2)	0.0262(8)	0.0163(7)	0.0167(7)	0.0042(6)	0.0025(6)	0.0028(6)
C(21)	2*i*		0.3136(2)	–0.2056(2)	0.0617(1)	0.0226(8)	0.0208(7)	0.0128(7)	0.0115(6)	0.0051(6)	0.0047(6)
C(22)	2*i*		0.4505(2)	–0.1296(2)	0.0884(2)	0.0237(8)	0.0201(7)	0.0208(7)	0.0113(6)	0.0077(6)	0.0095(6)
C(23)	2*i*		0.5382(2)	–0.1869(2)	0.1147(2)	0.0199(7)	0.0210(8)	0.0199(7)	0.0090(6)	0.0053(6)	0.0075(6)
C(24)	2*i*		0.4888(2)	–0.3186(2)	0.1151(2)	0.0248(8)	0.0237(8)	0.0207(8)	0.0145(7)	0.0074(6)	0.0096(6)
C(25)	2*i*		0.3503(2)	–0.3938(2)	0.0873(2)	0.0290(9)	0.0195(8)	0.0194(7)	0.0106(7)	0.0090(6)	0.0085(6)
C(26)	2*i*		0.2617(2)	–0.3395(2)	0.0598(2)	0.0208(8)	0.0216(8)	0.0195(7)	0.0089(6)	0.0079(6)	0.0064(6)
C(27)	2*i*		0.7657(2)	–0.1511(2)	0.1819(2)	0.0203(8)	0.0305(9)	0.047(1)	0.0121(7)	0.0060(8)	0.0180(9)
C(28)	2*i*		0.1760(2)	–0.5976(2)	0.0794(2)	0.035(1)	0.0280(9)	0.041(1)	0.0086(8)	0.0171(9)	0.0193(8)
C(31A)	2*i*	0.43(2)	0.657(2)	0.253(2)	0.460(2)	0.036(5)	0.052(8)	0.036(5)	0.013(6)	0.013(4)	0.026(5)
C(31B)	2*i*	0.36(2)	0.656(3)	0.273(2)	0.474(2)	0.044(8)	0.020(5)	0.046(8)	0.016(4)	–0.009(6)	0.010(5)
C(31C)	2*i*	0.176(4)	0.638(1)	0.314(1)	0.514(1)	0.031(6)	0.013(6)	0.032(7)	0.016(5)	0.013(5)	0.011(5)
Cl(1A)	2*i*	0.43	0.6266(5)	0.2932(8)	0.6039(6)	0.038(2)	0.069(2)	0.037(2)	0.025(2)	–0.002(1)	–0.003(2)
Cl(2A)	2*i*	0.43	0.6820(4)	0.1035(5)	0.4159(6)	0.049(1)	0.053(2)	0.032(2)	0.032(1)	–0.011(1)	–0.012(1)
Cl(1B)	2*i*	0.36	0.624(1)	0.277(2)	0.6132(8)	0.097(5)	0.116(6)	0.017(2)	0.083(5)	0.006(2)	0.002(3)
Cl(2B)	2*i*	0.36	0.6820(4)	0.134(1)	0.3913(6)	0.025(1)	0.092(5)	0.027(2)	0.017(2)	0.0014(9)	–0.003(2)
Cl(1C)	2*i*	0.176	0.5909(7)	0.2082(8)	0.5920(6)	0.044(2)	0.073(4)	0.025(3)	0.034(3)	0.018(2)	0.034(3)
Cl(2C)	2*i*	0.176	0.7131(8)	0.254(1)	0.4114(7)	0.086(4)	0.18(1)	0.079(4)	0.105(6)	0.065(4)	0.095(5)
N(1)	2*i*		–0.0447(1)	0.1455(1)	0.1236(1)	0.0188(6)	0.0163(6)	0.0154(6)	0.0081(5)	0.0049(5)	0.0030(5)
N(2)	2*i*		0.1415(1)	0.0261(1)	0.1521(1)	0.0165(6)	0.0176(6)	0.0166(6)	0.0070(5)	0.0059(5)	0.0041(5)
O(1)	2*i*		0.1007(1)	0.3564(1)	0.7619(1)	0.0249(6)	0.0315(7)	0.0188(6)	0.0097(5)	0.0113(5)	0.0103(5)
O(2)	2*i*		0.4983(1)	0.5994(1)	0.6889(1)	0.0203(6)	0.0212(6)	0.0161(5)	0.0026(5)	0.0040(4)	0.0015(4)
O(3)	2*i*		0.6709(1)	–0.1049(1)	0.1381(1)	0.0199(6)	0.0266(6)	0.0438(8)	0.0117(5)	0.0096(5)	0.0193(6)
O(4)	2*i*		0.3125(1)	–0.5220(1)	0.0902(1)	0.0303(7)	0.0234(6)	0.0429(8)	0.0117(5)	0.0142(6)	0.0193(6)

2. Tetrakis(3,5-dimethoxyphenyl)porphyrinato-copper(II) methylene chloride disolvate, $Cu(C_{52}H_{44}N_4O_8) \cdot 2CH_2Cl_2$

Table 4. Data collection and handling.

Crystal:	red block, size 0.44 × 0.495 × 0.52 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.08 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, φ/ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16715, 6129
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5978
$N(param)_{refined}$:	383
Program:	SHELXTL [5]

Table 5. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	2*i*		–0.1815	0.3457	0.1960	0.028
H(3)	2*i*		–0.0047	0.3798	0.3827	0.027
H(7)	2*i*		0.3201	0.1469	0.4473	0.026
H(8)	2*i*		0.3708	–0.0294	0.3016	0.026
H(12)	2*i*		0.0153	0.2047	0.5097	0.022
H(14)	2*i*		0.3344	0.5326	0.8173	0.021
H(16)	2*i*		0.3637	0.4198	0.4614	0.025
H(17A)	2*i*		–0.0921	0.2621	0.6508	0.057
H(17B)	2*i*		–0.0704	0.2513	0.7848	0.057
H(17C)	2*i*		–0.0370	0.1565	0.6732	0.057
H(18A)	2*i*		0.4909	0.7433	0.8351	0.035
H(18B)	2*i*		0.6407	0.7722	0.8335	0.035
H(18C)	2*i*		0.5602	0.6542	0.8739	0.035
H(22)	2*i*		0.4843	–0.0404	0.0871	0.024
H(24)	2*i*		0.5519	–0.3535	0.1347	0.025
H(26)	2*i*		0.1683	–0.3901	0.0403	0.025
H(27A)	2*i*		0.7618	–0.1566	0.2615	0.046
H(27B)	2*i*		0.8604	–0.0797	0.1995	0.046
H(27C)	2*i*		0.7501	–0.2391	0.1172	0.046
H(28A)	2*i*		0.1578	–0.5299	0.1492	0.051
H(28B)	2*i*		0.1679	–0.6740	0.0966	0.051
H(28C)	2*i*		0.1174	–0.6176	–0.0016	0.051
H(31A)	2*i*	0.48	0.5951	0.2480	0.3922	0.058
H(31B)	2*i*	0.48	0.7529	0.3338	0.4781	0.058
H(31C)	2*i*	0.31	0.5644	0.2606	0.4134	0.043
H(31D)	2*i*	0.31	0.7227	0.3590	0.4908	0.043
H(31E)	2*i*	0.180	0.5586	0.3182	0.4701	0.033
H(31F)	2*i*	0.180	0.7026	0.4070	0.5836	0.033

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		–0.1327(1)	0.1895(1)	0.0832(1)	0.0187(5)	0.0176(5)	0.0171(5)	0.0078(4)	0.0069(4)	0.0041(4)
C(2)	2*i*		–0.1277(1)	0.2970(1)	0.1944(1)	0.0274(6)	0.0230(6)	0.0173(6)	0.0145(5)	0.0070(5)	0.0040(5)
C(3)	2*i*		–0.0317(1)	0.3152(1)	0.2961(1)	0.0263(6)	0.0220(6)	0.0158(5)	0.0124(5)	0.0064(5)	0.0025(5)
C(4)	2*i*		0.0217(1)	0.2183(1)	0.2484(1)	0.0174(5)	0.0177(5)	0.0151(5)	0.0058(4)	0.0059(4)	0.0032(4)
C(5)	2*i*		0.1232(1)	0.2059(1)	0.3248(1)	0.0145(5)	0.0189(5)	0.0137(5)	0.0045(4)	0.0046(4)	0.0022(4)
C(6)	2*i*		0.1763(1)	0.1136(1)	0.2773(1)	0.0140(5)	0.0206(5)	0.0144(5)	0.0051(4)	0.0038(4)	0.0026(4)
C(7)	2*i*		0.2793(1)	0.0986(1)	0.3566(1)	0.0176(6)	0.0255(6)	0.0157(5)	0.0088(5)	0.0031(4)	0.0029(5)
C(8)	2*i*		0.3069(1)	0.0025(1)	0.2772(1)	0.0172(5)	0.0250(6)	0.0168(6)	0.0090(5)	0.0033(4)	0.0040(5)
C(9)	2*i*		0.2207(1)	–0.0421(1)	0.1488(1)	0.0143(5)	0.0194(5)	0.0162(5)	0.0054(4)	0.0044(4)	0.0044(4)
C(10)	2*i*		0.2188(1)	–0.1426(1)	0.0405(1)	0.0159(5)	0.0187(5)	0.0182(5)	0.0073(4)	0.0063(4)	0.0061(4)
C(11)	2*i*		0.1821(1)	0.2991(1)	0.4655(1)	0.0166(5)	0.0208(5)	0.0138(5)	0.0088(5)	0.0048(4)	0.0028(4)
C(12)	2*i*		0.1052(1)	0.2776(1)	0.5446(1)	0.0151(5)	0.0213(5)	0.0172(5)	0.0082(4)	0.0054(4)	0.0064(5)
C(13)	2*i*		0.1638(1)	0.3652(1)	0.6750(1)	0.0196(5)	0.0217(5)	0.0162(5)	0.0122(5)	0.0084(4)	0.0088(5)
C(14)	2*i*		0.2956(1)	0.4739(1)	0.7278(1)	0.0205(6)	0.0180(5)	0.0128(5)	0.0104(5)	0.0050(4)	0.0039(4)
C(15)	2*i*		0.3685(1)	0.4944(1)	0.6473(1)	0.0161(5)	0.0177(5)	0.0162(5)	0.0070(4)	0.0046(4)	0.0034(4)
C(16)	2*i*		0.3125(1)	0.4062(1)	0.5158(1)	0.0178(6)	0.0232(6)	0.0154(5)	0.0069(5)	0.0074(4)	0.0027(5)
C(17)	2*i*		–0.0354(2)	0.2477(2)	0.7140(2)	0.0228(7)	0.055(1)	0.0277(7)	0.0068(7)	0.0132(6)	0.0172(7)
C(18)	2*i*		0.5512(1)	0.7002(1)	0.8176(1)	0.0261(6)	0.0176(5)	0.0149(5)	0.0038(5)	0.0021(5)	0.0029(5)
C(21)	2*i*		0.3138(1)	–0.2049(1)	0.0612(1)	0.0207(6)	0.0200(5)	0.0135(5)	0.0102(5)	0.0057(4)	0.0045(4)
C(22)	2*i*		0.4507(1)	–0.1297(1)	0.0873(1)	0.0212(6)	0.0190(5)	0.0204(6)	0.0094(5)	0.0074(5)	0.0090(5)
C(23)	2*i*		0.5397(1)	–0.1858(1)	0.1142(1)	0.0189(6)	0.0218(6)	0.0201(6)	0.0090(5)	0.0071(5)	0.0094(5)
C(24)	2*i*		0.4915(1)	–0.3159(1)	0.1155(1)	0.0234(6)	0.0219(6)	0.0216(6)	0.0121(5)	0.0084(5)	0.0106(5)
C(25)	2*i*		0.3527(1)	–0.3904(1)	0.0881(1)	0.0268(6)	0.0180(5)	0.0199(6)	0.0090(5)	0.0093(5)	0.0081(5)
C(26)	2*i*		0.2627(1)	–0.3375(1)	0.0600(1)	0.0202(6)	0.0194(5)	0.0198(6)	0.0074(5)	0.0084(5)	0.0055(5)
C(27)	2*i*		0.7687(1)	–0.1484(2)	0.1824(2)	0.0200(6)	0.0326(7)	0.0435(8)	0.0139(6)	0.0083(6)	0.0196(7)
C(28)	2*i*		0.1790(2)	–0.5903(2)	0.0835(2)	0.0345(8)	0.0254(7)	0.0375(8)	0.0048(6)	0.0157(7)	0.0147(6)
C(31A)	2*i*	0.48(1)	0.666(1)	0.256(1)	0.462(1)	0.043(5)	0.075(5)	0.050(4)	0.033(3)	0.019(4)	0.042(4)
C(31B)	2*i*	0.31(1)	0.647(2)	0.268(1)	0.470(1)	0.016(4)	0.032(5)	0.050(8)	0.003(4)	–0.005(4)	0.022(5)
C(31C)	2*i*	0.180(3)	0.638(1)	0.312(1)	0.5166(9)	0.039(5)	0.031(5)	0.013(5)	0.014(4)	0.013(4)	0.008(4)
Cl(1A)	2*i*	0.48	0.6236(4)	0.2905(5)	0.6010(4)	0.044(1)	0.072(2)	0.037(2)	0.029(1)	–0.0052(9)	–0.006(1)
Cl(2A)	2*i*	0.48	0.6827(3)	0.1010(4)	0.4151(4)	0.0485(8)	0.061(1)	0.035(1)	0.0337(7)	–0.0110(7)	–0.0131(7)
Cl(1B)	2*i*	0.31	0.621(1)	0.268(1)	0.6115(8)	0.084(5)	0.145(7)	0.016(1)	0.089(5)	0.012(2)	0.012(3)
Cl(2B)	2*i*	0.31	0.6827(3)	0.137(1)	0.3879(4)	0.022(1)	0.096(4)	0.026(1)	0.015(1)	0.0028(7)	–0.001(1)
Cl(1C)	2*i*	0.180	0.5857(6)	0.2018(6)	0.5885(5)	0.038(2)	0.075(3)	0.031(3)	0.025(2)	0.012(2)	0.039(3)
Cl(2C)	2*i*	0.180	0.7144(5)	0.2559(8)	0.4115(5)	0.074(3)	0.158(6)	0.072(3)	0.090(4)	0.056(2)	0.086(4)
Cu(1)	1*a*		0	0	0	0.0123(1)	0.0150(1)	0.0123(1)	0.00440(8)	0.00385(7)	0.00176(8)
N(1)	2*i*		–0.0406(1)	0.1422(1)	0.1172(1)	0.0158(5)	0.0166(4)	0.0141(5)	0.0055(4)	0.0042(4)	0.0028(4)
N(2)	2*i*		0.1400(1)	0.0257(1)	0.1499(1)	0.0141(4)	0.0179(4)	0.0141(5)	0.0054(4)	0.0045(4)	0.0019(4)
O(1)	2*i*		0.1005(1)	0.3544(1)	0.76240(9)	0.0242(5)	0.0306(5)	0.0180(4)	0.0089(4)	0.0110(4)	0.0095(4)
O(2)	2*i*		0.49567(9)	0.5994(1)	0.68688(9)	0.0187(4)	0.0219(4)	0.0157(4)	0.0017(4)	0.0044(3)	0.0006(4)
O(3)	2*i*		0.6724(1)	–0.1046(1)	0.1371(1)	0.0178(4)	0.0264(5)	0.0414(6)	0.0105(4)	0.0087(4)	0.0193(4)
O(4)	2*i*		0.3156(1)	–0.5169(1)	0.0925(1)	0.0310(5)	0.0215(5)	0.0415(6)	0.0096(4)	0.0145(5)	0.0180(4)

3. Tetrakis(3,5-dimethoxyphenyl)porphyrinato-nickel(II) methylene chloride disolvate, $Ni(C_{52}H_{44}N_4O_8) \cdot 2CH_2Cl_2$

Table 7. Data collection and handling.

Crystal:	black block, size 0.38 × 0.41 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.66 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, φ/ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12672, 6071
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5640
$N(param)_{refined}$:	383
Program:	SHELXTL [5]

Table 8. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	2*i*		–0.1807	0.3439	0.1939	0.030
H(3)	2*i*		–0.0034	0.3786	0.3817	0.029
H(7)	2*i*		0.3172	0.1453	0.4470	0.031
H(8)	2*i*		0.3685	–0.0305	0.3013	0.030
H(12)	2*i*		0.0155	0.2044	0.5089	0.025
H(14)	2*i*		0.3367	0.5357	0.8186	0.023
H(16)	2*i*		0.3643	0.4197	0.4626	0.028
H(17A)	2*i*		–0.0916	0.2611	0.6482	0.060
H(17B)	2*i*		–0.0695	0.2527	0.7831	0.060
H(17C)	2*i*		–0.0355	0.1566	0.6727	0.060
H(18A)	2*i*		0.4948	0.7478	0.8376	0.040
H(18B)	2*i*		0.6450	0.7754	0.8369	0.040
H(18C)	2*i*		0.5631	0.6579	0.8767	0.040
H(22)	2*i*		0.4838	–0.0402	0.0873	0.025
H(24)	2*i*		0.5528	–0.3521	0.1363	0.027
H(26)	2*i*		0.1677	–0.3898	0.0418	0.027
H(27A)	2*i*		0.7658	–0.1536	0.2628	0.047
H(27B)	2*i*		0.8619	–0.0802	0.1975	0.047
H(27C)	2*i*		0.7489	–0.2404	0.1173	0.047
H(28A)	2*i*		0.1581	–0.5316	0.1504	0.055
H(28B)	2*i*		0.1671	–0.6763	0.0928	0.055
H(28C)	2*i*		0.1171	–0.6157	–0.0016	0.055
H(31A)	2*i*	0.483	0.5891	0.2420	0.3906	0.057
H(31B)	2*i*	0.483	0.7483	0.3318	0.4756	0.057
H(31C)	2*i*	0.25	0.5621	0.2703	0.4192	0.039
H(31D)	2*i*	0.25	0.7204	0.3691	0.5040	0.039
H(31E)	2*i*	0.249	0.7031	0.4081	0.5854	0.037
H(31F)	2*i*	0.249	0.5585	0.3173	0.4704	0.037

Table 9. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		–0.1318(1)	0.1879(1)	0.0813(1)	0.0212(6)	0.0185(6)	0.0182(6)	0.0093(5)	0.0090(5)	0.0051(5)
C(2)	2*i*		–0.1267(2)	0.2952(2)	0.1925(1)	0.0326(8)	0.0247(7)	0.0169(6)	0.0171(6)	0.0083(6)	0.0046(5)
C(3)	2*i*		–0.0306(2)	0.3138(2)	0.2947(1)	0.0304(8)	0.0239(7)	0.0162(6)	0.0149(6)	0.0083(6)	0.0039(5)
C(4)	2*i*		0.0227(1)	0.2170(2)	0.2468(1)	0.0205(6)	0.0203(6)	0.0147(6)	0.0081(5)	0.0078(5)	0.0039(5)
C(5)	2*i*		0.1230(1)	0.2055(2)	0.3247(1)	0.0164(6)	0.0233(7)	0.0135(6)	0.0066(5)	0.0064(5)	0.0027(5)
C(6)	2*i*		0.1741(1)	0.1125(2)	0.2762(1)	0.0160(6)	0.0269(7)	0.0147(6)	0.0085(5)	0.0054(5)	0.0033(5)
C(7)	2*i*		0.2766(2)	0.0972(2)	0.3559(1)	0.0207(7)	0.0342(8)	0.0151(6)	0.0138(6)	0.0048(5)	0.0032(6)
C(8)	2*i*		0.3043(2)	0.0014(2)	0.2767(1)	0.0197(7)	0.0325(8)	0.0164(6)	0.0133(6)	0.0048(5)	0.0040(6)
C(9)	2*i*		0.2182(1)	–0.0431(2)	0.1482(1)	0.0167(6)	0.0246(7)	0.0162(6)	0.0089(5)	0.0064(5)	0.0054(5)
C(10)	2*i*		0.2180(1)	–0.1427(2)	0.0415(1)	0.0184(6)	0.0209(6)	0.0179(6)	0.0089(5)	0.0080(5)	0.0066(5)
C(11)	2*i*		0.1826(1)	0.2994(2)	0.4659(1)	0.0194(6)	0.0266(7)	0.0132(6)	0.0126(6)	0.0064(5)	0.0034(5)
C(12)	2*i*		0.1059(1)	0.2779(2)	0.5443(1)	0.0185(6)	0.0257(7)	0.0175(6)	0.0119(5)	0.0072(5)	0.0074(5)
C(13)	2*i*		0.1652(2)	0.3667(2)	0.6751(1)	0.0253(7)	0.0259(7)	0.0169(6)	0.0178(6)	0.0119(5)	0.0100(5)
C(14)	2*i*		0.2975(2)	0.4761(1)	0.7287(1)	0.0270(7)	0.0204(6)	0.0130(6)	0.0153(6)	0.0076(5)	0.0050(5)
C(15)	2*i*		0.3705(1)	0.4963(2)	0.6490(1)	0.0201(6)	0.0207(6)	0.0163(6)	0.0113(5)	0.0057(5)	0.0039(5)
C(16)	2*i*		0.3132(2)	0.4066(2)	0.5168(1)	0.0206(7)	0.0287(7)	0.0150(6)	0.0113(6)	0.0086(5)	0.0032(5)
C(17)	2*i*		–0.0343(2)	0.2482(2)	0.7126(2)	0.0300(9)	0.060(1)	0.0289(9)	0.0147(8)	0.0183(7)	0.0198(8)
C(18)	2*i*		0.5547(2)	0.7037(2)	0.8204(1)	0.0355(8)	0.0185(7)	0.0150(6)	0.0079(6)	0.0035(6)	0.0029(5)
C(21)	2*i*		0.3134(2)	–0.2049(2)	0.0623(1)	0.0226(7)	0.0228(7)	0.0130(6)	0.0118(5)	0.0073(5)	0.0050(5)
C(22)	2*i*		0.4504(2)	–0.1294(2)	0.0880(1)	0.0238(7)	0.0215(7)	0.0212(7)	0.0117(6)	0.0086(5)	0.0107(5)
C(23)	2*i*		0.5401(2)	–0.1850(2)	0.1152(1)	0.0209(7)	0.0228(7)	0.0205(6)	0.0099(6)	0.0070(5)	0.0101(5)
C(24)	2*i*		0.4919(2)	–0.3148(2)	0.1169(1)	0.0267(7)	0.0226(7)	0.0216(7)	0.0138(6)	0.0091(6)	0.0106(5)
C(25)	2*i*		0.3528(2)	–0.3899(2)	0.0895(1)	0.0298(8)	0.0196(6)	0.0205(7)	0.0112(6)	0.0114(6)	0.0086(5)
C(26)	2*i*		0.2625(2)	–0.3371(2)	0.0614(1)	0.0224(7)	0.0216(7)	0.0194(6)	0.0088(5)	0.0098(5)	0.0054(5)
C(27)	2*i*		0.7700(2)	–0.1479(2)	0.1824(2)	0.0229(7)	0.0325(8)	0.044(1)	0.0157(7)	0.0092(7)	0.0201(7)
C(28)	2*i*		0.1789(2)	–0.5908(2)	0.0831(2)	0.0389(9)	0.0271(8)	0.039(1)	0.0061(7)	0.0198(8)	0.0150(7)
C(31A)	2*i*	0.483(9)	0.663(2)	0.252(1)	0.461(1)	0.040(5)	0.065(5)	0.055(4)	0.033(3)	0.015(3)	0.039(3)
C(31B)	2*i*	0.25(1)	0.644(2)	0.275(2)	0.474(2)	0.016(5)	0.041(9)	0.06(1)	0.015(6)	0.009(6)	0.037(9)
C(31C)	2*i*	0.249(5)	0.639(1)	0.312(1)	0.518(1)	0.037(5)	0.036(5)	0.019(5)	0.018(4)	0.012(3)	0.007(4)
Cl(1A)	2*i*	0.483	0.6235(4)	0.2886(4)	0.6007(4)	0.046(1)	0.065(2)	0.033(2)	0.028(1)	0.0004(9)	–0.007(1)
Cl(2A)	2*i*	0.483	0.6827(2)	0.0998(3)	0.4131(4)	0.0460(7)	0.060(1)	0.036(1)	0.0322(7)	–0.0079(6)	–0.0117(7)
Cl(1B)	2*i*	0.25	0.614(1)	0.253(2)	0.607(1)	0.091(6)	0.20(1)	0.028(3)	0.112(8)	0.033(4)	0.041(5)
Cl(2B)	2*i*	0.25	0.6836(3)	0.151(1)	0.3855(3)	0.026(1)	0.101(6)	0.024(1)	0.026(2)	0.0077(8)	0.012(2)
Cl(1C)	2*i*	0.249	0.5865(6)	0.2034(7)	0.5894(6)	0.035(1)	0.074(3)	0.039(2)	0.025(2)	0.013(1)	0.046(2)
Cl(2C)	2*i*	0.249	0.7175(5)	0.2574(8)	0.4113(5)	0.075(2)	0.138(5)	0.072(2)	0.085(3)	0.059(2)	0.081(3)
N(1)	2*i*		–0.0391(1)	0.1399(1)	0.1146(1)	0.0173(5)	0.0195(5)	0.0143(5)	0.0072(4)	0.0063(4)	0.0044(4)
N(2)	2*i*		0.1363(1)	0.0241(1)	0.1475(1)	0.0152(5)	0.0229(6)	0.0138(5)	0.0078(4)	0.0058(4)	0.0028(4)
Ni(1)	1*a*		0	0	0	0.0143(1)	0.0192(1)	0.0119(1)	0.0071(1)	0.00548(9)	0.00268(9)
O(1)	2*i*		0.1019(1)	0.3561(1)	0.7619(1)	0.0328(6)	0.0329(6)	0.0193(5)	0.0148(5)	0.0158(5)	0.0109(4)
O(2)	2*i*		0.4979(1)	0.6017(1)	0.6891(1)	0.0238(5)	0.0238(5)	0.0153(5)	0.0066(4)	0.0053(4)	0.0010(4)
O(3)	2*i*		0.6731(1)	–0.1036(1)	0.1381(1)	0.0197(5)	0.0267(6)	0.0432(7)	0.0115(4)	0.0094(5)	0.0200(5)
O(4)	2*i*		0.3162(1)	–0.5161(1)	0.0942(1)	0.0355(6)	0.0225(5)	0.0432(7)	0.0114(5)	0.0181(5)	0.0182(5)

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