Crystal structure of chloro-(5,10,15,20-tetraphenylporphyrinato)-manganese, $C_{44}H_{28}ClMnN_4$

Consuelo Yuste[I], Claudia C. Arranja[II], Mariana Marcos[II], Avula Balakrishna[II], Abilio J. F. N. Sobral[*, II] and Manuela Ramos Silva[*, I]

[I] CEMDRX, Physics Department, University of Coimbra, P-3004-516 Coimbra, Portugal
[II] Chemistry Department, University of Coimbra, P-3004 Coimbra, Portugal

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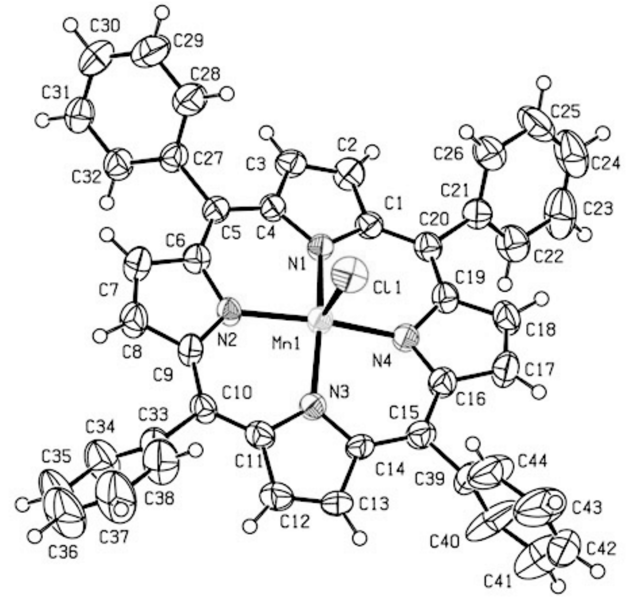

Abstract

$C_{44}H_{28}ClMnN_4$, monoclinic, $P2_1/c$ (no. 14), $a = 12.3044(6)$ Å, $b = 21.688(1)$ Å, $c = 17.0016(8)$ Å, $\beta = 123.536(3)°$, $V = 3781.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0645$, $wR_{ref}(F^2) = 0.0939$, $T = 293$ K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.10×0.12×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.55 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD area-detector, φ and ω
$2\theta_{max}$:	51.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	40354, 7243
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3202
$N(param)_{refined}$:	446
Programs:	SHELX [3], PLATON [4]

Source of material

Tetraphenylporphyrin (TPP) was synthesized from pyrrole (5 mL, 72 mmol) and benzaldehyde (8 mL, 70 mmol) following the procedure described by Adler et al. in 1967 [1]. Complexation with the metal was performed using manganese (II) chloride in dimethylformamide (80% yield), following the procedure described by Adler et al. in 1970 [2].

Experimental details

The structure was solved by direct methods. All H atoms were refined as riding on their parent atoms, with C–H=0.93-0.98Å, $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C) using SHELXL defaults [3]. There is a small amount of void space per unit cell which is filled with disordered solvent molecules. The intensity contribution of the disordered solvent molecules was removed by applying the SQUEEZE procedure in PLATON [4]. SQUEEZE estimated the electron counts in the voids of 315 Å^3 to be 87.

Discussion

This work is part of a project of synthesising porphyrins and porphyrin percursors [5-11]. Our aim is to obtain materials with *Single Chain Magnet* behaviour such as cyano bridged metalloporphyrins or multi-porous materials for CO_2 sequestring. In the title compound (Fig. 1) chloro-(5,10,15,20-tetraphenylporphyrinato)-manganese, the porphyrin moiety shows a saddle conformation with pairs of pyrrole β-C atoms alternately displaced above and below the porphyrin mean plane. The Mn(III) ion is penta-coordinated, and located 0.2663(8) Å above the plane formed by the four nitrogen atoms. The averaged manganese nitrogen distance is 2.005(4)Å. The phenyl rings are rotated nearly 60° with respect to the porphyrin ring except for the C39–C44 ring that is disordered, with torsion angles, C16–C15–C39B–C40B -80.9(11)° and C16–C15–C39A–C40A -88.9(15)°. The metallo-porphyrins assemble in pairs with the porphyrin planes nearly parallel, the Mn···Mn^i distance is 5.666(3) Å, i: -x+2, -y, -z. There are solvent acessible voids in the crystal structure that accomodate solvent molecules in a very disordered way, possibly two dimethylformamide molecules per unit cell. The crystal structures of the chloroform and acetone solvates are very similar to this one [12-13].

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	4*e*		0.6237	−0.0362	−0.1555	0.056
H(3)	4*e*		0.7567	−0.0926	−0.0085	0.052
H(7)	4*e*		1.1705	−0.0403	0.3297	0.060
H(8)	4*e*		1.3415	0.0371	0.3862	0.065
H(12)	4*e*		1.4096	0.2359	0.2351	0.067
H(13)	4*e*		1.2620	0.2999	0.0993	0.061
H(17)	4*e*		0.7624	0.2854	−0.1776	0.071
H(18)	4*e*		0.6081	0.1999	−0.2450	0.067
H(22)	4*e*		0.6241	0.0994	−0.3256	0.070
H(23)	4*e*		0.4230	0.0907	−0.4657	0.098
H(24)	4*e*		0.2449	0.0610	−0.4649	0.101
H(25)	4*e*		0.2658	0.0432	−0.3250	0.091
H(26)	4*e*		0.4635	0.0549	−0.1835	0.073
H(28)	4*e*		0.7734	−0.0615	0.1634	0.082
H(29)	4*e*		0.7440	−0.1526	0.2192	0.099

* Correspondence author (e-mail: manuela@pollux.fis.uc.pt)

Table 2. continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(30)	4*e*		0.8923	−0.2305	0.2702	0.077
H(31)	4*e*		1.0744	−0.2194	0.2644	0.064
H(32)	4*e*		1.1063	−0.1283	0.2088	0.058
H(34)	4*e*		1.5116	0.0636	0.3375	0.090
H(35)	4*e*		1.7135	0.0794	0.4732	0.129
H(36)	4*e*		1.7572	0.1642	0.5634	0.134
H(37)	4*e*		1.5946	0.2345	0.5226	0.129
H(38)	4*e*		1.3873	0.2185	0.3887	0.098
C(39A)	4*e*	0.473	1.019(2)	0.3160(6)	−0.048(1)	0.044(5)
C(40A)	4*e*	0.473	1.063(2)	0.3265(5)	−0.1032(8)	0.058(4)
H(40A)	4*e*	0.473	1.1052	0.2959	−0.115	0.070
C(41A)	4*e*	0.473	1.043(2)	0.3858(6)	−0.1432(8)	0.073(5)
H(41A)	4*e*	0.473	1.0744	0.3959	−0.1799	0.088
C(42A)	4*e*	0.473	0.975(1)	0.4282(8)	−0.127(1)	0.059(5)
H(42A)	4*e*	0.473	0.9584	0.4656	−0.1582	0.070

Table 2. continued.

Atom	Site	Occ.	x	y	z	U_{iso}
C(43A)	4*e*	0.473	0.930(1)	0.4229(6)	−0.072(1)	0.076(5)
H(43A)	4*e*	0.473	0.8891	0.4545	−0.0605	0.091
C(44A)	4*e*	0.473	0.951(1)	0.3619(6)	−0.034(1)	0.064(4)
H(44A)	4*e*	0.473	0.9182	0.3522	0.0028	0.077
C(39B)	4*e*	0.527	0.996(1)	0.3241(6)	−0.0422(9)	0.033(4)
C(40B)	4*e*	0.527	1.003(1)	0.3396(5)	−0.1174(7)	0.048(3)
H(40B)	4*e*	0.527	1.0158	0.3088	−0.1496	0.058
C(41B)	4*e*	0.527	0.992(1)	0.4017(6)	−0.1469(8)	0.058(4)
H(41B)	4*e*	0.527	0.9965	0.4124	−0.1978	0.070
C(42B)	4*e*	0.527	0.973(1)	0.4451(6)	−0.0976(9)	0.065(4)
H(42B)	4*e*	0.527	0.9590	0.4858	−0.1179	0.078
C(43B)	4*e*	0.527	0.974(1)	0.4301(4)	−0.017(1)	0.062(4)
H(43B)	4*e*	0.527	0.9648	0.4607	0.0168	0.075
C(44B)	4*e*	0.527	0.989(1)	0.3684(4)	0.011(1)	0.049(3)
H(44B)	4*e*	0.527	0.9931	0.3579	0.0658	0.059

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	4*e*	0.97953(6)	0.11652(3)	0.06608(4)	0.0362(4)	0.0336(4)	0.0323(4)	−0.0024(3)	0.0141(3)	−0.0003(3)
Cl(1)	4*e*	0.8793(1)	0.16842(5)	0.13173(8)	0.0650(9)	0.0566(8)	0.0622(9)	0.0002(6)	0.0384(7)	−0.0100(6)
N(1)	4*e*	0.8602(3)	0.0439(1)	0.0064(2)	0.035(2)	0.026(2)	0.033(2)	−0.006(2)	0.013(2)	−0.002(2)
N(2)	4*e*	1.1032(3)	0.0627(1)	0.1758(2)	0.030(2)	0.031(2)	0.030(2)	−0.002(2)	0.007(2)	−0.001(2)
N(3)	4*e*	1.1259(3)	0.1771(1)	0.1079(2)	0.035(2)	0.035(2)	0.036(2)	−0.002(2)	0.017(2)	0.001(2)
N(4)	4*e*	0.8748(3)	0.1610(1)	−0.0566(2)	0.034(2)	0.035(2)	0.034(2)	−0.007(2)	0.010(2)	0.001(2)
C(1)	4*e*	0.7489(4)	0.0398(2)	−0.0850(3)	0.037(3)	0.037(3)	0.034(3)	−0.006(2)	0.016(2)	−0.003(2)
C(2)	4*e*	0.6960(4)	−0.0210(2)	−0.0998(3)	0.049(3)	0.049(3)	0.031(3)	−0.009(2)	0.015(3)	−0.009(2)
C(3)	4*e*	0.7693(4)	−0.0520(2)	−0.0191(3)	0.043(3)	0.038(3)	0.043(3)	−0.013(2)	0.019(3)	−0.007(2)
C(4)	4*e*	0.8695(4)	−0.0123(2)	0.0477(3)	0.035(3)	0.031(3)	0.039(3)	−0.001(2)	0.016(2)	−0.002(2)
C(5)	4*e*	0.9609(4)	−0.0276(2)	0.1408(3)	0.038(3)	0.031(2)	0.040(3)	0.000(2)	0.019(3)	0.001(2)
C(6)	4*e*	1.0699(4)	0.0084(2)	0.2004(3)	0.042(3)	0.033(3)	0.040(3)	0.001(2)	0.024(3)	−0.003(2)
C(7)	4*e*	1.1702(4)	−0.0067(2)	0.2956(3)	0.058(3)	0.040(3)	0.041(3)	0.003(2)	0.021(3)	0.005(2)
C(8)	4*e*	1.2638(4)	0.0362(2)	0.3269(3)	0.048(3)	0.050(3)	0.038(3)	−0.002(3)	0.007(3)	0.003(3)
C(9)	4*e*	1.2236(4)	0.0800(2)	0.2537(3)	0.042(3)	0.033(3)	0.037(3)	0.005(2)	0.013(3)	0.003(2)
C(10)	4*e*	1.2957(4)	0.1305(2)	0.2592(3)	0.034(3)	0.037(3)	0.039(3)	−0.002(2)	0.012(2)	−0.004(2)
C(11)	4*e*	1.2509(4)	0.1743(2)	0.1894(3)	0.037(3)	0.044(3)	0.044(3)	−0.005(2)	0.019(3)	−0.003(2)
C(12)	4*e*	1.3223(4)	0.2275(2)	0.1901(3)	0.043(3)	0.049(3)	0.066(4)	−0.012(3)	0.025(3)	−0.002(3)
C(13)	4*e*	1.2417(4)	0.2627(2)	0.1153(3)	0.041(3)	0.043(3)	0.057(3)	−0.016(2)	0.020(3)	0.003(3)
C(14)	4*e*	1.1187(4)	0.2320(2)	0.0646(3)	0.039(3)	0.035(3)	0.040(3)	−0.009(2)	0.016(3)	0.003(2)
C(15)	4*e*	1.0073(4)	0.2553(2)	−0.0148(3)	0.047(3)	0.043(3)	0.043(3)	−0.009(2)	0.023(3)	0.000(2)
C(16)	4*e*	0.8918(4)	0.2225(2)	−0.0702(3)	0.043(3)	0.042(3)	0.040(3)	−0.006(2)	0.014(3)	0.002(2)
C(17)	4*e*	0.7760(4)	0.2456(2)	−0.1536(3)	0.056(3)	0.045(3)	0.044(3)	−0.005(3)	0.007(3)	0.010(2)
C(18)	4*e*	0.6914(4)	0.1985(2)	−0.1903(3)	0.039(3)	0.052(3)	0.047(3)	−0.001(3)	0.006(3)	0.003(3)
C(19)	4*e*	0.7506(4)	0.1460(2)	−0.1312(3)	0.041(3)	0.038(3)	0.040(3)	0.004(2)	0.019(3)	−0.001(2)
C(20)	4*e*	0.6942(4)	0.0876(2)	−0.1482(3)	0.037(3)	0.041(3)	0.033(3)	−0.002(2)	0.015(2)	−0.005(2)
C(21)	4*e*	0.5657(4)	0.0789(2)	−0.2388(3)	0.043(3)	0.037(3)	0.040(3)	−0.004(2)	0.018(3)	−0.004(2)
C(22)	4*e*	0.5517(5)	0.0887(2)	−0.3246(4)	0.057(4)	0.060(3)	0.048(4)	−0.003(3)	0.022(3)	−0.009(3)
C(23)	4*e*	0.4314(6)	0.0829(2)	−0.4088(4)	0.091(5)	0.064(4)	0.044(4)	0.011(3)	0.007(4)	−0.005(3)
C(24)	4*e*	0.3256(6)	0.0656(2)	−0.4084(4)	0.053(4)	0.077(4)	0.062(5)	0.000(3)	−0.005(4)	−0.015(3)
C(25)	4*e*	0.3384(5)	0.0552(2)	−0.3250(4)	0.032(4)	0.083(4)	0.087(5)	−0.006(3)	0.016(4)	−0.006(4)
C(26)	4*e*	0.4571(5)	0.0619(2)	−0.2399(3)	0.043(3)	0.073(3)	0.052(4)	−0.006(3)	0.018(3)	0.001(3)
C(27)	4*e*	0.9429(4)	−0.0857(2)	0.1783(3)	0.043(3)	0.033(3)	0.039(3)	−0.003(2)	0.019(3)	0.001(2)
C(28)	4*e*	0.8343(5)	−0.0930(2)	0.1830(3)	0.069(4)	0.055(3)	0.096(5)	0.010(3)	0.054(4)	0.022(3)
C(29)	4*e*	0.8174(5)	−0.1477(2)	0.2170(4)	0.085(4)	0.077(4)	0.109(5)	0.007(3)	0.068(4)	0.032(4)
C(30)	4*e*	0.9054(5)	−0.1943(2)	0.2473(3)	0.084(4)	0.043(3)	0.075(4)	0.002(3)	0.049(4)	0.012(3)
C(31)	4*e*	1.0138(4)	−0.1876(2)	0.2441(3)	0.061(4)	0.042(3)	0.052(3)	0.008(3)	0.028(3)	0.002(2)
C(32)	4*e*	1.0322(4)	−0.1330(2)	0.2101(3)	0.047(3)	0.037(3)	0.053(3)	0.003(2)	0.022(3)	0.003(2)
C(33)	4*e*	1.4275(4)	0.1405(2)	0.3479(3)	0.045(3)	0.038(3)	0.050(3)	−0.004(2)	0.011(3)	−0.003(2)
C(34)	4*e*	1.5267(5)	0.0983(2)	0.3743(4)	0.056(4)	0.074(4)	0.069(4)	0.001(3)	0.017(3)	−0.009(3)
C(35)	4*e*	1.6478(5)	0.1083(3)	0.4555(4)	0.049(4)	0.133(6)	0.082(5)	0.010(4)	−0.001(4)	−0.005(4)
C(36)	4*e*	1.6740(6)	0.1581(3)	0.5097(4)	0.064(5)	0.125(6)	0.077(5)	−0.015(4)	−0.005(4)	−0.023(4)
C(37)	4*e*	1.5777(6)	0.1998(3)	0.4854(4)	0.083(5)	0.092(5)	0.071(5)	−0.015(4)	−0.007(4)	−0.024(4)
C(38)	4*e*	1.4533(5)	0.1904(2)	0.4043(4)	0.076(4)	0.056(4)	0.070(4)	−0.005(3)	0.015(4)	−0.012(3)

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