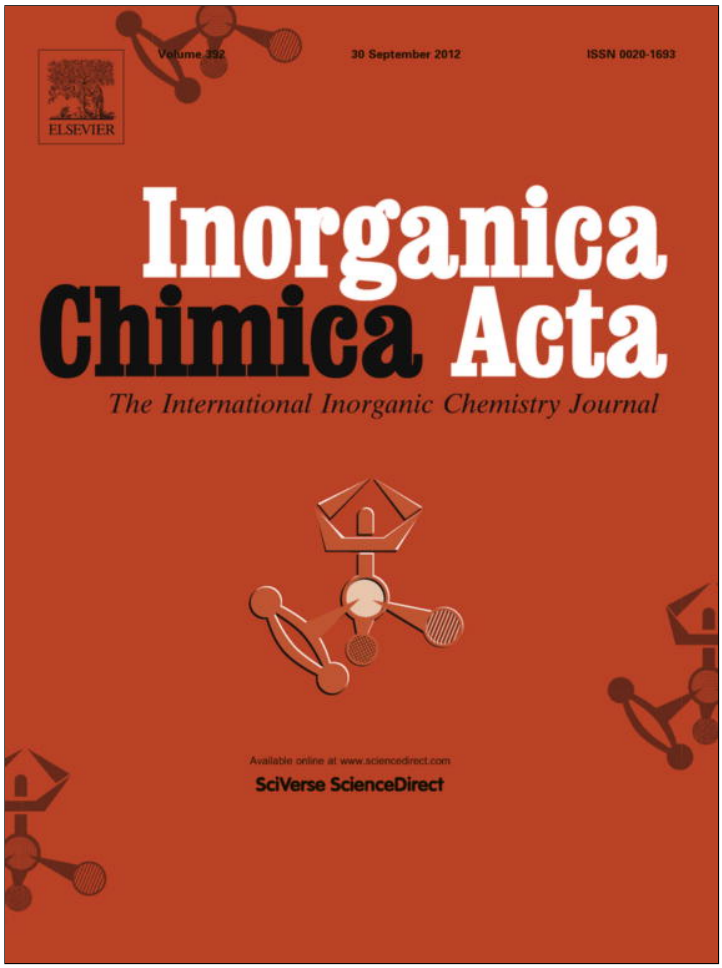

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Note

5,10,15,20-Tetra-*p*-phenylsulfonyporphinatocobalt(III), a water-soluble Co(III) porphyrin

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ABSTRACT

An alternative procedure is described for producing diffraction-quality crystals of the sodium salt of the water-soluble porphyrin diaqua-5,10,15,20-tetra-*p*-phenylsulfonyporphinatocobalt(III), $Na[Co(TPPS)(H_2O)_2]\cdot 4H_2O$ by vapour diffusion of ethyl acetate into an aqueous solution of the porphyrin overlaid with a layer of acetone. The structure contains a large amount of disordered solvent in channels but application of an appropriate algorithm (SQUEEZE – an algorithm incorporated into PLATON that applies a Fourier transform of the observed density in the solvent areas and incorporates its contribution to the structure factors) permits a structure solution.

1. Introduction

The metal complexes of the water-soluble synthetic porphyrin 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TTPS) have several interesting properties. For example, Mn(II)TTPS is a tumour-seeking MRI contrast agent [1,2]; Co(III)TTPS photocatalyses the oxidation of alcohols under anaerobic conditions [3] and has also been suggested as a useful cyanide scavenger [4]; and Fe(II)TTPS has been investigated as a peroxynitrite decomposition catalyst [5]. A great deal of work on the solution chemistry of these porphyrins has been carried out including, for example, the kinetics and thermodynamics of the substitution of coordinated H_2O in Cr(III)TTPS by imidazole [6,7], and by pyridine [8,9], I^- [10], SCN^- [9,10] and CN^- [4] in Co(III)TTPS, the kinetics of substitution of H_2O by CN^- in $[Ru(TPPS)(CO)(H_2O)]^{4-}$ [11], the reduction of Co(III)TTPS by Cr(II) [12], the dimerisation of Fe(III)TTPS [13], and the radiolytic [14,15] and electrochemical reduction of Co(III)TTPS [14]. Despite this interest, there is a single crystal structure of TTPS available in the Cambridge Structural Database [16], that of Ir(III) [17]. In this structure the counter ions are Na(benzo-18-crown-6)$^+$; the use of this particular crown ether was found to be essential to complex Na^+ and K^+ cations to produce diffraction-quality crystals. Powder patterns for $[Fe(TPPS)]^{3-}$ and $[Zn(TPPS)]^{4-}$ have been reported [18].

We report here conditions for the crystallisation of diaqua-5,10,15,20-tetrakis(4-sulfonatophenyl)porphinato-cobalt(III) in which Na^+ itself is the counter-ion. Despite the presence of a large amount of disordered solvent in the lattice, use of the SQUEEZE algorithm [19] allowed for a structure solution from the diffraction data.

2. Experimental

The preparation of CoTPPS was based on previous reports [9,20]. The free-base TPPS (Sigma–Aldrich) was contaminated by traces of the more hydrophobic di- and tri-substituted derivatives, as well as unidentified water-soluble salts. It was desalted using C18 Sep-Pak cartridges (Waters). We found this desalting step to be crucial for the successful crystallisation of the metalloporphyrin. Free-base TPPS (10 mg) was dissolved in slightly basic deionised water (ca. 2 mL; pH 9, NaOH) and refluxed with cobaltous acetate (100 M excess) under argon for 30 min in the dark. Thereafter, the reaction was cooled and stirred at room temperature for 3 h in air. The progress of the metallation was monitored by UV–Vis spectroscopy; the Soret band shifts from 413 to 425 nm. The resultant metalloporphyrin, which we shall refer to as CoTPPS, was precipitated out as dark pink flakes using cold acetone. The product gave a single peak on reverse phase HPLC.

Non-isothermal thermogravimetric analysis was performed on the crystalline CoTPPS (11.3040 mg) using a Q500 Thermogravimetric Analyzer V6.4 Build 193 at a heating rate of 10 °C min^{-1} from 10 to 600 °C under N_2. UV–Vis spectra were recorded on a Cary 300 Bio spectrometer and the temperature of the cell block was maintained with a Peltier device. NMR spectra were recorded on a Bruker 300 MHz spectrometer. Electrospray mass spectra were obtained on a Thermo Finnigan LXQ spectrometer operating in positive mode and visualised using Xcalibur 2.0.7.

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Table 1
Crystal data and structure refinement.

CCDC Deposition Number	868877
Molecular formula	$C_{44}H_{38}CoN_4NaO_{18}S_4$, $5(C_3H_6O)$, $C_4H_8O_2$
Formula weight	1469.41
T (K)	173(2)
λ (Å)	0.71073
Crystal system	tetragonal
Space group	$I4(1)/a$
Unit cell dimensions	
a (Å)	20.9614(3)
b (Å)	20.9614(3)
c (Å)	16.1294(5)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	7086.9(3)
Z	4
D_{calc} (Mg m^{-3})	1.405
Absorption coefficient (mm^{-1})	0.447
$F(000)$	3136
Crystal size (mm^3)	0.31 × 0.27 × 0.20
θ Range for data collection (°)	1.59–28.00
Index ranges	$-25 \le h \le 18$, $-27 \le k \le 27$, $-21 \le l \le 21$
Reflections collected	22782
Independent reflections	4280 [R_{int} = 0.0578]
Completeness to θ = 28.00° (%)	100.0
Absorption correction	None
Maximum and minimum transmissions	0.9159 and 0.8739
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4280/13/166
Goodness-of-fit (GOF) on F^2	1.093
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0661, wR_2 = 0.1850
R indices (all data)	R_1 = 0.0860, wR_2 = 0.1955
Largest difference in peak and hole (e Å^{-3})	0.675 and −0.747

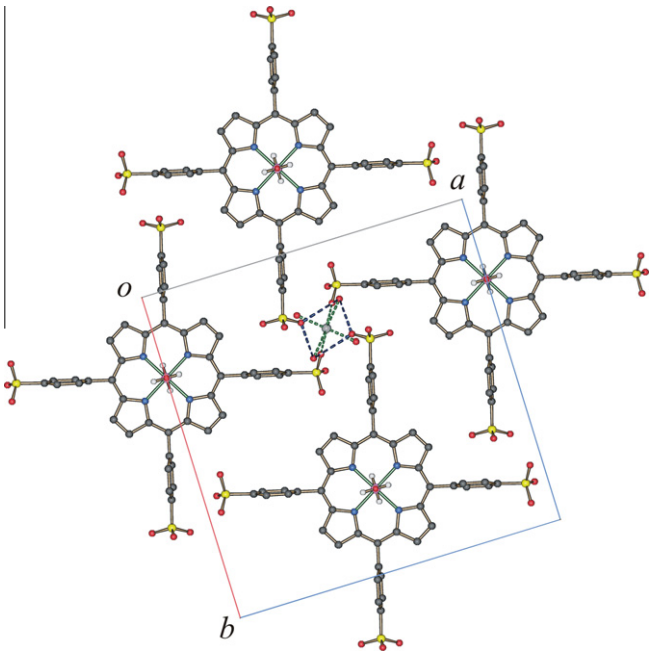

Fig. 1. View down the c axis of the unit cell of Na[Co(TTPS)(H_2O)]·4H_2O showing how the Na^+ ion interacts with four CoTPPS molecules.

CoTTPS: UV–Vis, pH 6, 25 °C, deionised water, λ_{max} (nm)/ε (10^4 M^{-1} cm^{-1}): 424/21.5; 537/1.13; 573(sh). ESI-MS (positive mode): 991.2 (CoTPPS$^+$ with loss of two H_2O ligands, base peak; calculated 990.99); 1013.22 (–H^++Na^+, 15%; calculated 1012.97); 1035.35 (–2H^++2Na^+, 4%; calculated 1034.96). ^{1}H (MeOD, ppm relative to TMS at 300 MHz, room temperature): 9.099 (singlet, β H of porphyrin); 8.257 (doublet of doublets; phenyl H); integration ratio 1:2. The sharp NMR resonances confirm the metal is in the diamagnetic +3 oxidation state and paramagnetic Co(II) porphyrins give very broad resonances [21,22].

To produce diffraction-quality crystals, a saturated CoTPPS solution (ca. 0.1 g in 0.5 mL deionised water, pH 6.89, 25 °C) was added into one arm of an H-tube. Cold acetone was carefully added as a layer above this solution very slowly so as not to disturb the saturated CoTPPS layer. Ethyl acetate was added to the other arm of the H-tube, sealed under argon and stored in the dark at 4 °C. Deep purple-red rhomboid-shaped crystals were observed after about 2 weeks. The crystalline material produced was routinely stored at 4 °C. We were unable to produce diffraction-quality material using any other method, including vapour diffusion of acetone into an aqueous solution of CoTTPS.

Intensity data were collected on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50 kV, 30 mA) using the APEX 2 (Bruker, 2005) data collection software [23]. The collection method involved ω-scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the programme SAINT+ SAINT+ [24]. The crystal structure was solved by direct methods using SHELXTL [25]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Publication materials were generated using SHELXTL, PLATON [19] and SCHAKAL-99 [26].

The structure contains a large number of disordered solvent molecules in solvent channels. An analysis of the solvent accessible voids in the structure using PLATON indicates that the volume occupied by the solvent channels accounts for about 44% of the total volume of the structure. Consequently, the data were processed using the SQUEEZE algorithm [27] included in PLATON [19] which accounted for 849 electrons in the unit cell. This number of electrons could correspond to approximately 84.9 H_2O molecules, or 26.5 acetone molecules (boiling point 56–57 °C), or 17.7 ethyl acetate (boiling point 77.1 °C) molecules per unit cell, but is likely to be mixture of these due to the crystallisation procedure used. A TGA analysis of the sample indicates that solvent is easily lost at room temperature, indicating that the contents of the solvent channel are very volatile. Of the crystallisation solvents used, acetone has the lowest boiling point and is the most volatile. Taking these considerations into account, we have assumed the dominant component in the solvent channel to be acetone, and to account for the 849 electrons required, have assumed that the channels are occupied by 20 acetone and 4 ethyl acetate molecules per unit cells which conveniently leads to a number divisible by Z. The contribution of 20 acetone molecules and 4 ethyl acetate molecules (total 832 electrons) has been added to $F(000)$, the crystal density, as well as the chemical formula.

3. Results and discussion

Details of the crystal data and the structure refinement are given in Table 1; further details are given in the Supplementary information. The compound crystallised in the space group $I4_1/a$ with four molecules in the unit cell (Fig. 1). Four sulfonyl groups from neighbouring molecules are bridged by Na^+ ions, with Na^+ disordered equally over two positions. It is bonded ionically to a sulfonyl group on two neighbouring molecules through O3 (Fig. 2), and then to four O5 atoms to form a distorted octahedral

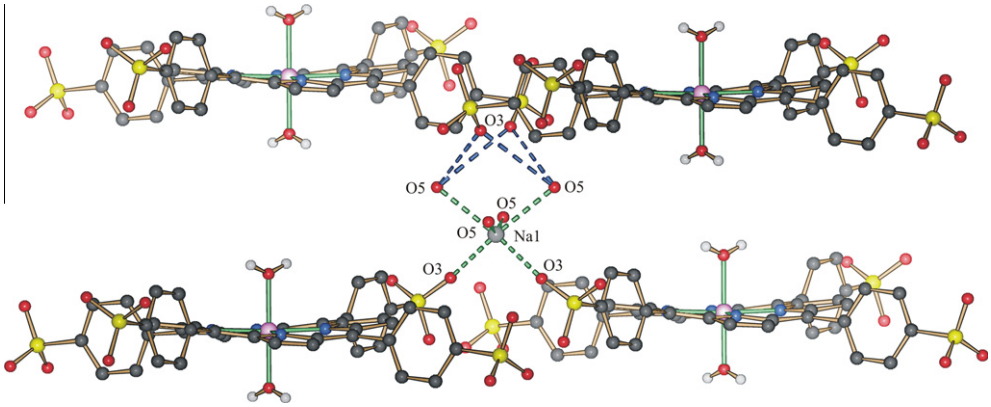

Fig. 2. Na^+ and four H_2O molecules bridge four sulfonyl groups of neighbouring porphyrins. Two sulfonyl groups are ionised and the other two are protonated and hydrogen bonded to water O5. The Na^+ ion is disordered over two positions, only one of which is illustrated.

Table 2
Co(III) porphyrins with at least one axial ligand.

Porphyrin	CCSD REFCODE	Axial ligands, L, and Co–L bond length (Å)		Co–N_{porph} (Å)		Ref.
5,10,15,20-Tetraphenylporphyrin	BEKPIQ	H_2O	1.940	1.958	1.959	[30]
		H_2O	1.932	1.967	1.970	
5,10,15,20-Tetraphenylporphyrin	EFITIW	H_2O	2.114	1.954	1.960	[31]
		NO_2	1.863	1.966	1.977	
5,10,15,20-Tetraphenylporphyrin	GAMTAP	H_2O	1.978	1.950	1.955	[32]
		Cl	2.216	1.958	1.958	
5,10,15,20-Tetrakis(2-(pivaloylamino)phenyl)porphyrin	WAKYUD	H_2O	1.996	1.973	1.975	[33]
		NO_2	1.890	1.976	1.978	
5,10,15,20-Tetramethylchiroporphyrin	WIDZAK	H_2O	1.930	1.909	1.915	[34]
		H_2O	1.937	1.918	1.922	
5,10,15,20-Tetraphenylporphyrin	XEGRIK	H_2O	1.963	1.981	1.981	[35]
		NO_2	1.963	1.984	1.984	

coordination environment. This coordinated unit then hydrogen bonds to a sulfonyl group of two other neighbouring molecules resulting in an environment of four sulfonyl groups around each Na^+ leading to a three-dimensional coordination structure. Consequently, the formula is one Na^+ per molecule and two of the sulfonyl groups of each porphyrin moiety are protonated. It was not possible to place the missing hydrogen atoms for the sulfonyl and O5 since the protons are disordered but their contribution has been accounted for in $F(000)$, as well as in the chemical formula. There are channels through the crystal structure which contain the disordered solvent molecules (Figs. S2a and S2b).

The porphyrin core is in a saddled D_{2d} conformation [28] with the meso carbon atoms approximately in the mean plane through the metal and the 24 atoms of the porphyrin core (Fig. S1 of the Supplementary information), and the C_β carbons that form the outer edge of each pyrrole ring alternately displaced above and below the mean porphyrin plane. The Co–N bond lengths are 1.971(2) Å and the bond length between Co(III) and the axial H_2O ligands is 1.947(3) Å.

There are six Co(III) porphyrin structures in the Cambridge Structural Database in which at least one of the axial ligands is H_2O (Table 2). In one, the porphyrin core is planar (XEGRIK) and the average Co–N bond length is 1.983(2) Å; four have D_{2d} ruffled symmetry (GAMTAP, WAKYUD, BEKPIQ, WIDZAK), with Co–N = 1.95(2) Å. There is one example of a saddled structure (EFITIW) with Co–N = 1.967(11) Å. The present structure therefore has very similar bond lengths to the porphyrin donor atoms. The average Co–O bond length to coordinated H_2O trans to H_2O of the structures in Table 2 is 1.935(5) Å, which is not significantly different to the value of 1.947(3) Å in the present structure.

Because of crystal packing forces, meso phenyl groups in porphyrins are often tilted and not perpendicular to the mean porphyrin plane [29]. In the present structure, the phenyl rings are nearly perpendicular to the mean plane through the 25 atoms of the corrin core (84.9°), probably because of the interaction of the sulfonyl moieties with the Na^+ ions (Fig. 2), which bridges four neighbouring porphyrin molecules.

Three events occur during the TGA procedure (Fig. S3): between 25 and 100 °C (mass loss 15%); between 200 and 300 °C (6% mass loss); and between 525 and 575 °C (a further 16% mass loss). The crystal structure shows that the material consists of repeating units of $Na[Co(TTPS)(H_2O)_2]\cdot 4H_2O$ in which two of the sulfonic acid moieties are protonated and a large amount of disordered solvent in channels, accounting for 44% of the unit cell volume. This disordered solvent is likely to consist of acetone, ethyl acetate and water because of the crystallisation procedure used (see above), and according to SQUEEZE accounts for approximately 849 electrons per unit cell. This number of electrons might correspond to 84.9 H_2O molecules (1529.6 atomic mass units (amu) per unit cell), or 26.5 acetone molecules (1540.9 amu per unit cell), or 17.7 ethyl acetate molecules (1558.3 amu per unit cell), giving an average of 1542 amu due to solvent per unit cell. There are four porphyrin moieties in the unit cell, giving a total mass of 4480 amu. Thus, the disordered solvent comprises approximately 26% of the mass of the material. It seems likely that the loss of much of this solvent corresponds to the first feature in the TGA thermogram, although this only accounts for 15% mass loss. This suggests that a significant amount of the solvent is volatile and readily lost from the material at room temperature. The second feature probably corresponds to loss of water associated with the Na^+ counter ions (approximately

6.4% of the mass and in good agreement with the observed mass loss of 6.0%). The high temperature feature is likely to arise from decomposition of the sample.

4. Conclusions

An alternative and simpler procedure for the crystallisation of the water-soluble porphyrin $[Co(TPPS)(H_2O)_2]^-$ without use of a crown ether to order Na^+ ions is reported. Although the structure contains a large amount of disordered solvent molecules, application of a suitable algorithm allows for a structure solution. This procedure may be useful for crystallising derivatives of these porphyrins.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.05.021.

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