

Synthesis, structural and spectroscopic characterization of the bis(nitrito-*N*) octaethylporphyrin cobalt(III) complex

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ABSTRACT

The bis(nitrito-*N*) cobalt(III) octaethylporphyrin derivative with the formula $[\text{K}(\text{18-C-6})(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2 [\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$ (**1**) (OEP = octaethylporphyrin and 18-C-6 is the ether 18-crown-6) has been synthesized and characterized by UV-vis, IR and proton NMR spectroscopy which indicate, inter alia, that the cobalt ion presents the oxidation state III. The synthesis utilizes 18-crown-6 to solubilize potassium nitrite in the synthetic procedure. This compound crystallizes in the triclinic system, with the centric space group P-1 and the following unit cell parameters: $a = 11.6724(2) \text{ \AA}$, $b = 12.5715(2) \text{ \AA}$, $c = 13.4722(3) \text{ \AA}$, $\alpha = 101.1290(6)^\circ$, $\beta = 106.6498(6)^\circ$, $\gamma = 109.1507(6)^\circ$, $Z = 1$ and $V = 1696.74(5) \text{ \AA}^3$. The crystal structure has been solved and refined to $R = 0.0499$ and $R(w) = 0.1319$. The X-rays molecular structure of **1** shows that there is a relatively close interaction of both two NO_2^- axial ligands of the ion complex $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$ with the potassium atoms of the two counterions $[\text{K}(\text{18-C-6})(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]^{0.5+}$. The title compound exhibits one-dimension polymer-like structure where "monomers" are linked together through strong $\text{O}(\text{H}_2\text{O})\cdots\text{O}(\text{nitrito-O})$ hydrogen bonds.

Keywords: Cobalt(III) Porphyrin; X-Rays Diffraction; UV-Visible; ¹H NMR

1. INTRODUCTION

We have previously reported our observations on the reactions of nitrite ion with iron(III) porphyrinates [1-3]. The reactions with iron(III) porphyrin derivatives having open (unprotected) faces, e.g., OEP or TPP derivatives [4], lead to complicated reactions in which coordinated nitrite is attacked by uncoordinated nitrite to yield, inter alia, nitrosyl derivative [5]. The instability of the nitrite-iron(III) system with open-faced porphyrins was overcome by the use of a protected pocket derivative, *i.e.*,

picket fence porphyrin. We also showed [6] that the reaction of the iron(II) picket fence starting material $[\text{Fe}^{\text{II}}(\text{TpivPP})]$ with an excess of potassium nitrite and cryptand-222 in chlorobenzene yields the five-coordinated mono-nitrito-*N* species $[\text{Fe}^{\text{II}}(\text{TpivPP})(\text{NO}_2)]^-$. On the other hand many X-rays crystal structures of nitrito-*N* cobalt(III) porphyrin complexes have been reported since 1970; seven of them with the TPP porphyrin [7-12] and four with the TpivPP porphyrin [13,14]. Studying these species aimed specially the understanding of oxo-transfer reactions involved in many catalytic organic reactions [15,16]. All these species present either the nitrito-*N* as sole axial ligand *i.e.*, $[\text{Co}^{\text{III}}(\text{TPP})(\text{NO}_2)]$ [7] or together with a σ -donor neutral ligand, *i.e.*, $[\text{Co}^{\text{III}}(\text{TPP})(\text{NO}_2)(\text{EtOH})]$ [9] and $[\text{Co}^{\text{III}}(\text{TpivPP})(\text{NO}_2)(1\text{-MeIm})]$ [14]. There is no indication in the literature of either a nitrito-*N* cobalt derivative with the octaethylporphyrin (OEP) or a bis(nitrito-*N*) cobalt species with any kind of porphyrin. One possible reason for the latter observation is synthetic limitations. The reported syntheses make use of organic-soluble cobalt porphyrins and the water-soluble KNO_2 inorganic salt which are effectively incompatible reactants. We report in this paper the use of crown ether 18-C-6 to solubilize KNO_2 salt in chlorobenzene solvent used with cobalt metalloporphyrins. This synthetic procedure leads to the stable bis(nitrito-*N*) octaethylporphyrin cobalt(III) derivative. Hence, this paper reports the synthesis, the spectroscopic characterization and single crystal X-ray structure of $[\text{K}(\text{18-C-6})(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2 [\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$ (**1**).

2. EXPERIMENTAL

2.1. Materials and Methods

Potassium nitrite salt KNO_2 was recrystallized twice from hot distilled water, dried under vacuum overnight at about 70°C and stored under argon. The crown ether 18-C-6 was recrystallized from toluene, dried under vacuum and stored under argon in the dark. Chlorobenzene was purified by washing with sulfuric acid and distilled over P_2O_5 . Hexanes

and toluene were distilled from their sodium-benzophenone solution under a nitrogen atmosphere. All other reagents and solvents employed were commercially available and were used as received without further purification. UV-visible spectra were recorded on a SHIMADZU UV-2401 spectrometer and Fourier-transformer IR data on a SHIMADZU FTIR-8400 spectrometer. ^1H NMR spectra were obtained at room temperature on a Bruker 300 Ultrashield spectrometer.

2.2. Synthesis of



Potassium nitrite (350 mg, 4.11 mmol) and crown ether 18-C-6 (200 mg, 0.57 mmol) were stirred together in chlorobenzene (10 mL). 100 mg (0.17 mmol) of $[\text{Co}^{\text{II}}(\text{OEP})]$ [17,18], dissolved in chlorobenzene (10 mL), were added to the nitrite/crown solution and stirred at 35°C overnight. X-ray-quality crystals were obtained by slow diffusion of hexanes into the chlorobenzene solution. UV-Vis ($\text{C}_6\text{H}_5\text{Cl}$); λ_{max} [nm]: 425, 536, 569. ^1H NMR (CDCl_3 , ppm): 10.14(m, H-*meso*), 4.0(m, $-\text{CH}_2-$), 7.2(m, $-\text{CH}_3$). IR (KBr , v/cm^{-1}): 1462, 1313, 820 (NO_2^-), 1110 ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$). Anal. Calc. (Found) for $\text{C}_{60}\text{H}_{94}\text{CoK}_2\text{N}_7\text{O}_{19}$: C, 53.20 (54.08); H, 6.99 (6.87); N, 7.24 (7.30).

2.3. X-Ray Diffraction

Single crystal X-ray diffraction measurements were carried out at 293 K on a Bruker Nonius FR590 Kappa CCD area detector diffractometer employing graphite monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in the ϕ/ω scan mode. Final unit cell dimensions were refined on the entire data set. Integration and scaling resulted in the data set were corrected for Lorentz and polarization effects using DENZO/SCALEPACK [19]. Intensities were corrected for absorption with the program SORTAV-2000 [20]. The minimum and the maximum transmission factors values are 0.913 and 0.981, respectively. The trial structure was obtained by direct methods using SIR-2004-1.0 [21], which revealed the position of the cobalt and potassium atoms, most atoms of the porphyrinato ligand, and the crown ether 18-C-6. The remainder of the structure was found in the subsequent difference Fourier syntheses. One ethyl group of the OEP porphyrin is disordered over two orientations (C17A-C18A and C17B-C18B) with refined occupancy coefficients converged to 0.794(9) and 0.206(9), respectively. The anisotropic displacement ellipsoids of the O9, O10 and N4 atoms of the nitrito-*O* ligand and the oxygen O11 of the water molecule (both ligands alternatively coordinated to each potassium ion) were very elongated which indicates static disorder. For these atoms the SIMU/ISOR restraints command [22] in the SHELXL-97 [23] software was used.

The final structural refinement was made against F^2

data with the program SHELXL-97. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms (except those of the water molecule) were localized by idealization methods and were allowed to ride upon the respective carbon atoms. Crystal data and experimental parameters used for the intensity data collection are summarized in **Table 1**.

3. RESULTS AND DISCUSSION

3.1. UV-Visible and IR

The electronic spectra of complex 1 and the $[\text{Co}^{\text{II}}(\text{OEP})]$ starting compound are represented in **Figure 1**. The Soret absorption band of the latter compound shifts from 391 nm to 425 nm upon nitrito-*N* coordination. The Soret bands for cobalt(II) octaethylporphyrins are around 390 nm while those of cobalt(III) octaethylporphyrin derivatives are around 420 nm (**Table 2**). Thus the UV-vis technique indicates that complex 1 is a Co(III) porphyrin species.

Complex 1 shows a strong absorption band in the IR spectrum at 1110 cm^{-1} attributed to the $-\text{CH}_2-\text{O}-\text{CH}_2-$ group of the counterion $[\text{K}(\text{18-C-6})(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]^{0.5+}$. It has been noticed [26] that nitrito-*N* metal transition complexes exhibit $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ in the 1470 - 1370 and 1340 - 1320 cm^{-1} regions respectively and $\delta(\text{NO}_2)$ near 800 cm^{-1} while nitrito-*O* complexes exhibit two well separated stretching NO_2 frequencies $\nu(\text{N}=\text{O})$ and $\nu(\text{N}-\text{O})$ at 1485 - 1400 and 1110 - 1050 cm^{-1} , respectively. Our cobalt(III) bis(nitrito-*N*) derivative presents three absorption bands at 1462, 1313 and 820 cm^{-1} attributed to a nitrito-*N* ligand.

3.2. Proton NMR Spectroscopy

The paramagnetic starting material $[\text{Co}^{\text{II}}(\text{OEP})]$ species (with the ground configuration $3d^7$) presents downfield chemical shifts of the *meso*-hydrogens (β (H-*meso*) = 29.60 ppm) (**Table 3**). Goff and co-workers were surprised to notice that penta-coordinated Co(II) species type $[\text{Co}^{\text{II}}(\text{OEP})(\text{L})]$ (L = monodentate neutral axial ligand) derivatives show hydrogens $\beta(\text{H-}i\text{meso})$ in the region of diamagnetic OEP species ($\sim 9 - 10$ ppm) [27]. Chemical shift of H-*meso* protons for diamagnetic $3d^6$ penta-coordinated and hexa-coordinated cobalt(III) porphyrin species are in the 10 - 11 ppm region. Complex 1 exhibits H-*meso* peaks at 10.70 ppm which indicates that this species corresponds most probably to a cobalt(III) porphyrinate. The spectrum of 1 exhibits a resonance peak at 2.75 ppm attributed to the $-\text{CH}_2-\text{O}-\text{CH}_2-$ group of the 18-crown-6.

3.3. Crystal Structure

The asymmetric unit of the structure contains one cobalt(III) ion coordinated to a half octaethylporphyrin molecule and a nitrito-*N* ligand which is also coordinated,

Table 1. Crystal data and refinement parameters for $[\text{K}(\text{18-C-6})(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$.

Empirical formula	$\text{C}_{60}\text{H}_{94}\text{N}_7\text{O}_{19}\text{K}_2\text{Co}$
Formula weight, ($\text{g}\cdot\text{mol}^{-1}$)	1354.56
<i>Crystal system</i>	triclinic
<i>Space group</i>	<i>P-1</i>
<i>Lattice constants</i>	
<i>a</i> (Å)	11.6724(2)
<i>b</i> (Å)	12.5715(2)
<i>c</i> (Å)	13.4722(3)
α (°)	101.1390(6)
β (°)	106.6498(6)
γ (°)	109.1507(6)
Volume <i>V</i> (Å ³)	1696.74(5)
<i>Z</i>	1
<i>D</i> _{cal} , g/cm^3	1.326
Absorption coefficient, μ (mm^{-1})	0.449
<i>F</i> (000)	720
Crystal size (mm^3)	$0.40 \times 0.20 \times 0.20$
<i>T</i> (K)	293(2)
θ -range for data collection	3.19 - 29.65
Limiting indices	$-16 \leq h \leq 15, -17 \leq k \leq 14$ $-17 \leq l \leq 18$
<i>Completeness</i> (%)	97.5
<i>T</i> _{min} / <i>T</i> _{max}	0.913/0.981
<i>Reflections collected/unique</i>	26800/9348
<i>R</i> (int)/ <i>R</i> (sigma)	0.0335/0.0485
<i>Data/restraints/parameters</i>	9348/42/440
<i>Goodness-of-fit on F</i> ²	1.053
<i>Final R indices</i> [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0499, wR_2 = 0.1319$
<i>R indices (all data)</i>	$R_1 = 0.0823, wR_2 = 0.1499$
<i>Largest peak and hole</i> ($e\text{Å}^{-3}$)	0.675 and -0.563

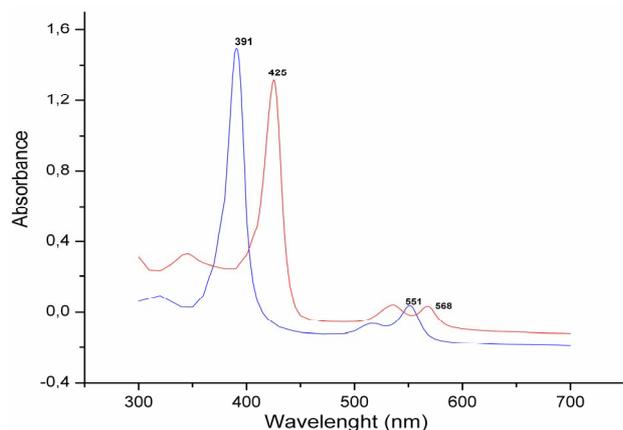


Figure 1. UV-visible spectra of $[\text{Co}^{\text{II}}(\text{OEP})]$ starting material (blue spectrum) and $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$ (red spectrum). The spectra were taken in chlorobenzene at room temperature.

Table 2. Electronic spectra data for selected cobalt octaethylporphyrins.

Complex	λ_{max} (nm)			Ref.
	Soret band	β	α bands	
<i>Cobalt(II) porphyrins</i>				
$[\text{Co}^{\text{II}}(\text{OEP})]^{\text{a}}$	391	516	551	This work
$[\text{Co}^{\text{II}}(\text{OEP})(\text{pip})]^{\text{b}}$	396	518	545	[24]
<i>Cobalt(III) porphyrins</i>				
$[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^{\text{a}}$	425	536	569	This work
$[\text{Co}^{\text{III}}(\text{OEP})(\text{pip})_2]^{\text{b}}$	421	535	568	[24]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{Me}_2\text{SO})_2]^{\text{b}}$	424	536	556	[24]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^{\text{a}}$	429	543	573	[25]

^aIn chlorobenzene solvent; ^bin methylene chloride solvent.

Table 3. ^1H NMR data for the OEP free-base and some cobalt octaethylporphyrins.

Complex	(H- <i>meso</i>)	-CH ₂	-CH ₃	Ref.
OEP ^a	10.11	4.12	1.93	This work
$[\text{Co}^{\text{II}}(\text{OEP})]^{\text{a}}$	29.60	8.80	5.10	This work
$[\text{Co}^{\text{II}}(\text{OEP})(\text{py})]^{\text{b}}$	9.30	3.60	2.99	[27]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^{\text{a}}$	10.14	4.00	1.98	This work
$[\text{Co}^{\text{III}}(\text{OEP})(\text{Cl})]^{\text{b}}$	10.83	3.93	1.81	[28]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{I})]^{\text{b}}$	10.52	3.91	1.79	[28]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^{\text{a}}$	10.69	4.14	1.93	[25]

^aIn CDCl_3 solvent; ^bin C_6D_6 solvent.

through the two oxygen atoms, to a potassium ion. This cation is also coordinated to a 18-crown-6 molecule and alternatively (50%/50%) to a water molecule and a nitrito-*O* ligand. **Figure 2** is an ORTEP diagram of the ion complex $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$ which shows that the cobalt ion is coordinated to the four nitrogen atoms of the porphyrin and the nitrogens of the two nitrito-*N* axial ligands.

Figure 3 displays a most interesting feature of **1**; the interaction of the $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]^{0.5+}$ cation with the $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$ anion. Complex **1** presents relatively close interaction of both nitrito-*N* axial ligands of the $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$ anion with the potassium ions of the two counterions $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]^{0.5+}$. Thus the potassium ion is coordinated to both oxygen atoms O1 and O2 of the nitrite ion with K-O1 and K-O2 distances of 3.019(2) Å and 3.055(2) Å respectively (**Table 4**). This structure presents a striking resemblance with the one of the bis(nitrito-*N*) iron(III) picket fence porphyrin which has the formula $[\text{K}(18\text{-C-}6)(\text{H}_2\text{O})][\text{Fe}^{\text{III}}(\text{TpivPP})(\text{NO}_2)_2]$ [1]. For this iron(III) species, the potassium ion of the $[\text{K}(18\text{-C-}6)(\text{H}_2\text{O})]^+$ counterion is coordinated to the oxygen atoms of the NO_2^- axial ligand situated in the side of the picket fence porphyrin. The crystallographically unique K-O distance is 2.929(14) Å. For the other related species $[\text{K}(18\text{-C-}6)(\text{NO}_2)][\text{Fe}^{\text{II}}(\text{TpivPP})(\text{NO})]$ [3], the K-O(nitrito-*O*) distances are 2.877(14) Å and 2.798(14) Å. Thus, in the current case, the K-O(nitrito-*O*) bond length is slightly longer than those just mentioned above. Unfortunately there are no further examples of K-O(NO_2) distances to compare with but we can say that for complex **1**, there is a real coordination bond between the potassium cation and the NO_2^- anion which is also coordinated to the cobalt(III).

Each potassium ion is alternatively coordinated to a water molecule and a nitrito-*O* group (50%/50% of probability). The K-O10 bond length (2.726(8) Å) is normal for K-O(water) distances and the K-O9 bond length (3.001(8) Å) is within observed K-O(nitrito-*O*) distances following our earlier discussion. The equatorial bonding features of the potassium ion with the 18-crown-6 macrocycle appear normal with an average K-O distance of 2.823(2) Å. The potassium ion is slightly displaced toward the two oxygens O1 and O2 of the NO_2^- ligand coordinated to the cobalt ion.

One dimension polymer-like structure is also depicted in **Figure 3** where the $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$ "monomers" are linked together by quite strong O-H...O hydrogen bond (2.836(12) Å) between the oxygen O10 of the H_2O ligand (coordinated to the potassium ion) and the oxygen O9 of the nitrito-*O* ligand, which is coordinated to the potassium ion of an adjacent "monomer". The comparison of Co-N(NO_2) bond lengths

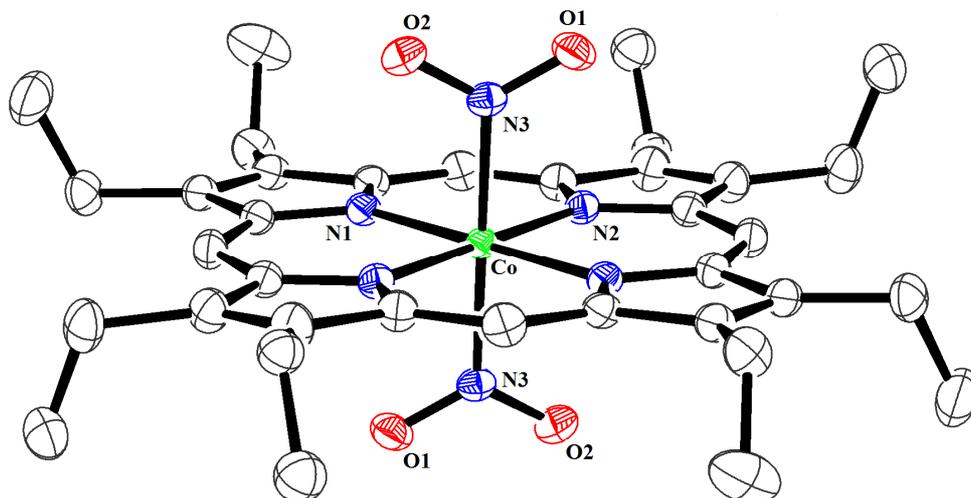


Figure 2. ORTEP view of the ion complex $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$, thermal ellipsoids are drawn at the 30% probability level. Only the major positions of the disordered atoms are shown and hydrogen atoms have been omitted for clarity.

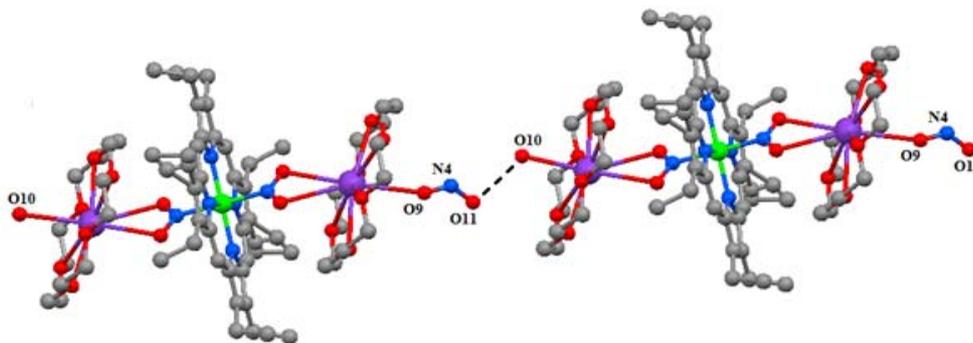


Figure 3. Schematic representation of two $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$ "monomers" linked together by hydrogen bond.

Table 4. Selected bond lengths (Å) and angles (°) of $[\text{K}(18\text{-C-}6)(\text{NO}_2)_{0.5}(\text{H}_2\text{O})_{0.5}]_2[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]$.

Cobalt coordination polyhedron			
Co-N1	1.991(2)	Co-N3	1.968(2)
Co-N2	1.985(2)	N1-Co-N2	90.67(6)
Co-Np	1.988(2)	N1-Co-N3	88.07(6)
N2-Co-N3	90.85(6)		
Nitrito-N ligand			
N3-O1	1.234(2)	N3-O2-K	97.7(1)
N3-O2	1.233(2)	N3-O1-K	99.4(1)
O1-N3-O2	119.2(2)	Co-N3-O1	120.2(1)
Co-N3-O2	120.6(1)		
Potassium coordination polyhedron			
K-O1	3.019(2)	K-O6	2.806(2)
K-O2	3.055(2)	K-O7	2.852(2)
K-O3	2.731(1)	K-O8	2.849(2)
K-O4	2.809(2)	K-O9	3.001(8)
K-O5	2.894(2)	K-O10	2.726(8)

of several nitrito-*N* Co(III) porphyrins (**Table 5**) shows that the ion complex $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$ presents the longest value (1.968(2) Å) which indicates a weak interaction between the NO_2^- axial ligand and the Co(III) metal ion. This could be explained by the coordination of each nitrito-*N* axial ligand to a potassium ion which causes lengthening of the nitrogen of the NO_2^- group from the cobalt(III).

For all nitrito-*N*-iron porphyrinates, the nitrite ligand bisects the $\text{N}_p\text{-Fe-N}_p$ bond angles to within a few degrees. This orientation is not the result of steric interactions, but apparently strongly reflects a feature in the bonding interaction of nitrite with iron [6]. The nitrite ligand and not the heme determines the orientation of the two $d\pi$ orbitals of Fe^{2+} to achieve the best π overlap. In other words, the lobes of the two $d\pi$ orbitals are parallel and perpendicular to the nitrite plane. Thus, for the $[\text{Fe}^{\text{II}}(\text{TpivPP})(\text{NO}_2)]^-$ [6], the dihedral angle between the nitrite ligand and the nearest Fe- N_p vector is 40.4°. In all nitrito-*N*-cobalt porphyrin species (**Table 5**), we also notice that the NO_2^- ligand bisects the $\text{N}_p\text{-Co-N}_p$ bond angles to within

a few degrees. For the newly synthesized complex ion $[\text{Co}^{\text{III}}(\text{OEP})(\text{NO}_2)_2]^-$, the dihedral angle between the nitro plane and the nearest Co- N_p vector is 38.5°. It is well established that for Fe(II) and Fe(III) porphyrins, the mean porphyrin equatorial iron pyrrole nitrogen distance Fe- N_p is related to the oxidation state and the spin state of the iron [33]. For Co(II) and Co(III) porphyrin complexes, the relationship between the Co- N_p distance and the oxidation and the spin states is not obvious. Nevertheless, it has been noticed [34] for these species, that ruffling in porphyrin complexes always results in a shortening of the M- N_p bonds. It is noteworthy that the OEP porphyrin core presents much less distortions than those of *meso*-porphyrins such as TPP or TpivPP. Thus, for the very ruffled structures $[\text{Co}^{\text{II}}(\text{TPP})]$ [29] and $[\text{Co}^{\text{III}}(\text{TpivPP})(\text{N}_3)_2]^-$ [25], the Co- N_p bond length values are 1.923(4) Å and 1.964(4) Å respectively while the very slightly ruffled structure $[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^-$ [25] presents a Co- N_p distance of 1.984(2) Å. The Co- N_p distance of complex 1 (1.988(2) Å) is normal for a cobalt not ruffled OEP species.

Table 5. Porphyrinato core parameters (Å) for selected Co(II) and Co(III) porphyrin complexes.

Complex	Co- N_p^a	Co- X_L^b	Ref.
$[\text{Co}^{\text{II}}(\text{TPP})]$	1.923(4)	-	[29]
$[\text{Co}^{\text{II}}(\text{TpivPP})]$	1.966(3)		[14]
$[\text{Co}^{\text{II}}(\text{OEP})]$	1.971(3)	-	[17]
$[\text{Co}^{\text{II}}(\text{OEP})(\text{NO})]$	1.984(8)	1.8444(9)	[30]
$[\text{Co}^{\text{II}}(\text{OEP})(\text{DMAP})]$	1.982(2)	2.191(2) ^c	[31]
Co(III) porphyrin complexes			
$[\text{Co}^{\text{III}}(\text{TPP})(\text{py})]$	1.985(4)	2.155(3) ^d	[27]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{CN})_2]^-$	1.986(3)	1.915(4) ^e ; 1.927(4) ^e	[32]
$[\text{Co}^{\text{III}}(\text{OEP})(\text{N}_3)_2]^-$	1.984(2)	1.965(3) ^f ; 1.984(3) ^f	[25]
$[\text{Co}^{\text{III}}(\text{TpivPP})(\text{N}_3)_2]^-$	1.964(4)	1.944(6) ^f	[25]
Co(III) nitrito- <i>N</i> porphyrin complexes			
$[\text{Co}^{\text{III}}(\text{TPP})(\text{NO}_2)]$	1.956(3)	1.880(3) ^g	[7]
$[\text{Co}^{\text{III}}(\text{NO}_2)(\text{PPh}_3)]$	1.943(6)	2.000(7) ^g ; 2.424(2) ⁱ	[10]
$[\text{Co}^{\text{III}}(\text{TPP})(\text{NO}_2)(\text{py})]$	1.969(4)	1.921(4) ^g ; 2.032(4) ^d	[12]
$[\text{Co}^{\text{III}}(\text{TPP})(\text{NO}_2)(\text{H}_2\text{O})]$	1.967(8)	1.863(8) ^g ; 2.114(8) ^j	[11]
$[\text{Co}^{\text{III}}(\text{TpivPP})(\text{NO}_2)(1\text{-MeIm})]$	1.964(4)	1.899(4) ^g ; 1.994(4) ^k	[12]
$[\text{Co}^{\text{III}}(\text{TpivPP})(\text{NO}_2)(1,2\text{-Me}_2\text{Im})]$	1.983(4)	1.917(4) ^g ; 2.090(4) ^l	[12]

^aAverage equatorial iron-nitrogen pyrrole distance; ^bCobalt-axial ligand distance; ^cCo-N(DMAP) distance; ^dCo-N(py) distance; ^eCo-C(CN) distance; ^fCo-N(azide) distance; ^gCo-N(NO_2) distance; ⁱCo-(PPh_3) distance; ^jCo-O(H_2O) distance; ^kCo-N(1-MeIm) distance; ^lCo-N(1,2-Me₂Im) distance.

4. CONCLUSIONS

We have used the synthetic strategy of crown-ether-solubilized potassium nitrite to increase the concentration of nitrite ion in the chlorobenzene organic solvent preparation which yields the bis(nitrito-*N*) cobalt(III) octaethylporphyrin derivative. The novel $[K(18-C-6)(NO_2)_{0.5}(H_2O)_{0.5}]_2[Co^{III}(OEP)(NO_2)_2]$ complex was characterized by UV-Vis, IR and 1H NMR spectroscopies which indicate that our synthetic Co(III) derivative is a cobalt(III) octaethylporphyrin species. The X-ray molecular structure of **1** is very interesting showing (1) that the two NO_2^- axial ligand, coordinated to the Co^{3+} of the ion complex $[Co^{III}(OEP)(NO_2)_2]^-$, present strong interactions with the potassiums of the two counterions $[K(18-C-6)(NO_2)_{0.5}(H_2O)_{0.5}]^{0.5+}$, (2) the complex **1** exhibits one-dimension polymer-like structure where “monomers” are linked together through strong O-H(H_2O)...O(NO_2^-) hydrogen bonds.

5. SUPPLEMENTARY MATERIAL

Crystallographic data for the title compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-807653). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +441,223/336,033; mailto: deposit@ccdc.cam.ac.uk.

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- Abbreviations used in this paper: Porph; a generalized porphyrin dianion, TPP; dianion of the 5,10,15,20-tetra-phenylporphyrin, TpivotPP; dianion of $\alpha, \alpha, \alpha, \alpha$ -terakis(*o*-pivalamidophenyl) porphyrin (picket fence porphyrin), OEP; dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, cryptand-222; 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8,8,8]hexacosane, 18-C-6; 1,4,7, 10,13,16-hexaoxacyclooctadecane (18-crown-6), DMAP; 4-(*N,N'*-dimethylamino) pyridine. 1-Melm; 1-methylimidazole, 1-2-Me2Im; 1,2-dimethylimidazole, pip; piperidine.
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