2 H; CH$_2$), 1.68 (m, 1 H; CH), 1.10 (s, 3 H; CH$_3$), 1.05 (s, 3 H; CH$_3$), and 0.95 (s, 3 H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 204.5$, 178.2, 170.1, 166.6, 90.9, 67.9, 54.9, 54.3, 51.9, 46.6, 38.1, 30.7, 30.5, 28.9, 16.6, 16.4 and 9.7; ES-MS (+ve mode): [M^++Na] 363.2 (100), 283.5 (18), 239.1 (20); HRMS calcd for $C_{17}H_{24}O_7$: 340.1522, found: 341.1580 [M^++H].

(*S*,*S*)-**10**; The preparation of this compound is as described for (*R*,*S*)-**10**. Starting material (*R*,*S*)-**9** (13.3 mg, 0.03 mmol) was used and the product was obtained as colorless crystals (9 mg, 85.6 %). M.p. = 92 – 93 °C; R_f = 0.19; IR (Nujol): $\tilde{\nu} = 2940$, 1810, 1755 (s. broad), 1722, 1190, 1164, 1120, 950 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 5.70$ (m, 1 H; CH), 3.69 (s, 3 H; CH$_3$), 2.98 (dd, $J = 17.3$ and 7 Hz, 1 H; CH), 2.86 (dd, $J = 17.3$ and 5.5 Hz, 1 H; CH), 2.77 (dd, $J = 15.8$ and 5.5 Hz, 1 H; CH), 2.70 (dd, $J = 15.8$ and 6.3 Hz, 1 H; CH), 2.40 (m, 1 H; CH), 2.20 (s, 3 H; CH$_3$), 1.95 (m, 2 H; CH$_2$), 1.68 (m, 1 H; CH), 1.10 (s, 3 H; CH$_3$), 1.05 (s, 3 H; CH$_3$), and 0.95 (s, 3 H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 204.4$, 178.2, 170.1, 166.6, 90.9, 67.8, 54.8, 54.3, 51.9, 46.6, 38.0, 30.7, 30.5, 28.9, 16.6, 16.4 and 9.7; ES-MS (+ve mode): [M^++Na] 363.0 (100), 283.5 (8), 238.9 (20); HRMS calcd for $C_{17}H_{24}O_7$: 340.1522, found: 341.0980 [M^++H].

Crystal Data for *(S,S)*-**9**: $C_{20}H_{30}O_6S_2$, $M_r = 430.56$, Orthorhombic space group $P2_12_12_1$, $a = 6.3432(13)$, $b = 16.713(3)$, $c = 20.190(4)$ Å, $U = 2140.4(7)$ Å^3, $Z = 4$, $\mu(\text{Mo}_{K\alpha}) = 0.282$ mm^{-1}, 5375 unique data were produced from 15601 measured reflections ($R_{\text{int}} = 0.0891$), $R_1 = 0.0535$ and $wR_2 = 0.1172$.

Crystal Data for *(S,S)*-**10**: $C_{17}H_{24}O_7$, $M_r = 340.36$, Monoclinic space group $P2_1$, $a = 6.175(2)$, $b = 7.547(2)$, c = 19.027(4) Å, $\beta = 98.44(3)°$, $U = 877.1(3)$ Å^3, $Z = 2$, $\mu(\text{Mo}_{K\alpha}) = 0.1$ mm^{-1}, 3611 unique data were produced from 16126 measured reflections ($R_{\text{int}} = 0.0987$), $R_1 = 0.0528$ and $wR_2 = 0.1179$. CCDC-166921 (*(S,S)*-**9**) and CCDC-127009 (*(S,S)*-**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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A New Mononuclear Iron(III) Complex Containing a Peroxocarbonate Ligand[**]

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Peroxo iron(III) complexes have been proposed as key intermediates in various oxidation reactions catalyzed by mononuclear non-heme iron enzymes and their functional model complexes.[1] Various types of synthetic mononuclear peroxo – iron(III) complexes with η^2-peroxo,[2, 3] η^1-hydroperoxo,[3, 4] and alkylperoxo[5] ligands have been characterized by spectroscopic studies. However, there is no structurally characterized mononuclear peroxo iron(III) complex to date. It has been shown that the structure, electronic structure, and reactivity of the peroxo complexes can be modified by the coordination environment at an iron(III) center. For instance, a tetradentate tripod ligand, tris(2-pyridylmethyl)amine (TPA), has been shown to form a low-spin η^1-hydroperoxo species, whereas sterically bulky TPA derivatives with 6-methyl groups give low-spin and/or high-spin alkylperoxo species.[5d] Furthermore, interconversion between η^2-peroxo and η^1-hydroperoxo species has been also observed in some complexes, where a change in spin states (high spin and low spin) also occurs.[1c, 3] Most of these peroxo – iron(III) complexes have nitrogen-rich coordination environments, except for the ethylenediaminetetraacetate (EDTA) complex. Thus, it is of interest to investigate how the nature of the donor atoms and the stereochemistry of the supporting ligands influence the formation, structure, and properties of such peroxo – iron(III) complexes. Here, we report the synthesis of a novel mononuclear iron(III) complex with a bidentate peroxocarbonate ligand in a carboxylate-rich coordination environment, [Fe(qn)$_2$(O$_2$C(O)O)]Ph$_4$P · 1.5 CH$_3$OH · 0.5 (CH$_3$)$_2$NCHO (**1**; see Figure 1), derived from the reaction of a bis(μ-hydroxo)diiron(III) complex, [Fe$_2$(qn)$_4$(OH)$_2$] · 2 H$_2$O (**2**) with H$_2$O$_2$ and CO$_2$, where Hqn is quinaldic acid. Compound **1** is the first

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example of a crystallographically characterized transition metal complex with a peroxocarbonate ligand.

Reaction of **2** with an excess of hydrogen peroxide (>10 equivalents) in the presence of 2 equivalents of 1,8-diazabicyclo[5,4,0]-7-undecene (DBU) or tetra-*n*-butylammonium acetate ($n\mathrm{Bu_4N(OAc)}$) in dimethylformamide (DMF) at −60 °C, gave a deep blue solution.[6] This solution is not thermally stable even at −60 °C and decomposed to give a reddish yellow solution under air. It was found that the decomposition was much accelerated under a CO_2 atmosphere, which suggests that CO_2 plays an important role in the decomposition of the blue species. The electrospray ionization (ESI) mass spectrum of the reddish yellow reaction mixture, in the range of *m*/*z* 150 to 1200, showed a signal at *m*/*z* 476 (relative intensity (I) = 100 %) which matches well with the calculated isotopic distribution for the complex ion, $[\mathrm{Fe(qn)_2(O_2C(O)O)}]^-$ (see Supporting Information, Figure S1). Complex **1** is thermally unstable and decomposed to give a yellow species in DMF within 1 h at 0 °C.

The complex anion of **1** has a distorted octahedral structure with a *trans*-N_2O_4 donor set composed of a bidentate peroxocarbonate and two bidentate qn ligands (Figure 1). The peroxocarbonate forms a five-membered chelate ring with the O1-Fe-O3 angle of 78.8(1)°. The O1−O2 bond length is 1.455(5) Å, which is comparable to those of $\mathrm{KH(O_2C(O)O)\cdot H_2O_2}$ (1.457(2) Å)[7] and a perketyl platinum complex (1.46 Å),[8], and in the range of those of alkylperoxo transition metal complexes (1.36–1.52 Å).[9] This bond length is longer than the corresponding lengths in *cis*-μ-1,2-peroxo diiron(III) complexes (1.406(8)–1.426(6) Å)[10] and comparable to those of μ_4-peroxo hexa-iron(III) complexes (1.47–1.48 Å).[11] The Fe−O1 bond length (1.936(3) Å) is intermediate between the average Fe−O bond length of the *cis*-μ-1,2-peroxo diiron(III) complexes (1.89 Å) and μ_4-peroxo hexairon(III) complexes (2.04 Å). The Fe-O1-O2 angle (115.0(2)°) in **1** is comparable to those of μ_4-peroxo hexairon(III) complexes (113–116°) and smaller than those of *cis*-μ-1,2-peroxo diiron(III) complexes (118.1–129.5°). The C−O bond lengths (C1–O2, C1–O3, and C1–O4) of the peroxocarbonate ligand are 1.378(7), 1.282(6), and 1.236(7) Å, respectively, which are also similar to those of $\mathrm{KH(O_2C(O)O)\cdot H_2O_2}$ (1.381(2), 1.249(2), and 1.229(2) Å).[7] The short C1−O4 bond length suggests double bond character.

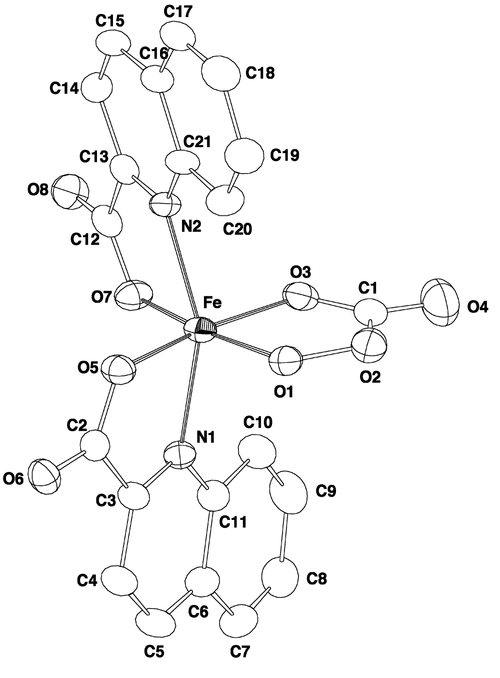

Figure 1. ORTEP view (thermal ellipsoids at 50 % probability) of the anion of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe-O1 1.936(3), Fe-O3 1.999(3), Fe-O5 1.983(3), Fe-O7 1.993(3), Fe-N1 2.178(4), Fe-N2 2.186(4), O1-O2 1.455(5), C1-O2 1.378(7), C1-O3 1.282(6), C1-O4 1.236(7); O1-Fe-O3 78.8(1), O1-Fe-O5 88.3(1), O1-Fe-O7 166.9(1), O1-Fe-N1 93.6(1), O1-Fe-N2 106.0(1), O3-Fe-O5 167.1(1), O3-Fe-O7 88.4(1), O3-Fe-N1 103.0(1), O3-Fe-N2 94.9(1), O5-Fe-O7 104.5(1), O5-Fe-N1 78.1(1), O5-Fe-N2 88.2(1), O7-Fe-N1 86.4(1), O7-Fe-N2 77.8(1), N1-Fe-N2 155.8(1), Fe-O1-O2 115.0(2), O1-O2-C1 112.2(4).

The electron paramagnetic resonance (EPR) spectrum of a frozen DMF–ethanol solution of **1** at 78 K showed a signal at $g = 4.3$, arising from a high-spin iron(III) center (see Supporting Information, Figure S2). The electronic spectrum of **1** in DMF at −60 °C (Figure 2) shows an intense absorption band at 440 nm ($\varepsilon = 1450\,\mathrm{M^{-1}\,cm^{-1}}$), which may be assigned to the ligand to metal charge transfer (LMCT) transition from the peroxocarbonate ligand (π_v^* orbital of the peroxo moiety) to the iron(III) center (dπ orbital). The corresponding LMCT transitions of the mononuclear hydroperoxo[3, 4] and alkylperoxo[5] iron(III) complexes, irrespective of their spin state (low spin or high spin), have been observed at 506–640 nm. Thus, the LMCT transition energy of **1** is substantially blue-shifted relative to those of the other complexes. For fuller understanding of such a significant blue-shift of the LMCT transition, further study is needed.

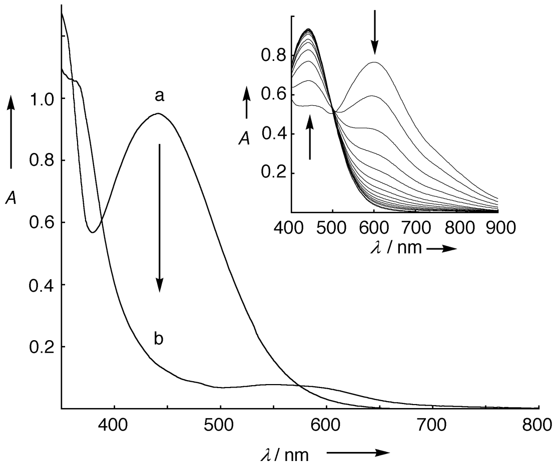

Figure 2. Electronic spectra of **1** (a) in DMF ([Fe] = 0.64 mM) at −60 °C and its decomposed species (b) at room temperature. Inset: spectral change for the formation of **1** by flowing CO_2 over the deep blue solution, generated by the reaction of **2** in DMF ($[\mathrm{Fe_2}]$ = 0.33 mM) with 10 equivalents of H_2O_2, in the presence of 2 equivalents of DBU, at −60 °C. The spectra were measured by an optical-fiber apparatus with a corrected light path length of 1.03 cm.

The resonance Raman spectrum of **1**, measured in DMF at approximately −60 °C with a 514.5 nm laser excitation, showed five isotope sensitive bands at 965, 884, 728, 578, and 547 cm^{-1}, which were shifted to 946 ($\Delta\nu = -19$), 841

($\Delta\nu = -43$), 710 ($\Delta\nu = -18$), 564 ($\Delta\nu = -14$), and 524 cm^{-1} ($\Delta\nu = -23$) by use of ^{18}O (Compare Figure 3a and b).[12] The band at 965 cm^{-1} is also isotope sensitive; a sample prepared by use of $^{13}CO_2$ showed a band at 960 cm^{-1} ($\Delta\nu = -5$; Figure 3c), which indicates that CO_2 is the carbon source of the peroxocarbonate ligand. No significant shifts were observed for the other bands (0–2 cm^{-1}). The band at 884 cm^{-1} is assigned to the $\tilde{\nu}$(O–O) stretching vibration, as the magnitude of shift to lower wavenumber by ^{18}O substitution is -43 cm^{-1} (-50 cm^{-1} for diatomic harmonic oscillators), which compares well with those of the peroxo complexes. Unlike **1**, the Raman spectra of the alkylperoxo iron(III) complexes in a high-spin state exhibit two bands at around 880 cm^{-1} and 840 cm^{-1}, attributed to a significant mixing of the ν(O–O) and ν(C–O) vibrations of the alkylperoxo groups. It is noted that the infrared spectra of $[RhCl(O_2C(O)O)(PEt_2Ph)_3]$ (**3**) showed the ν(O–O) band at 963 cm^{-1} ($\Delta\nu = -20$ cm^{-1}) reported by Aresta et al.,[13] which is shifted to a significantly higher wavenumber than that of **1**. The isotope labeling experiments of **3** revealed that the formation of the peroxocarbonate ($^{18}O-^{16}O-C(^{16}O)^{18}O$) proceeds through ^{18}O–^{18}O bond cleavage of the η^2-peroxo ligand and $C^{16}O_2$ insertion. Unlike **3**, the formation of the peroxocarbonate unit in **1** appears to proceed by a nucleophilic addition of a peroxo group to CO_2 without the O–O bond cleavage, because the isotope labeling experiments showed a large $\Delta\nu$ value (-43 cm^{-1}), and there is no $\nu(^{16}O-^{18}O)$ band between 884 cm^{-1} ($\nu(^{16}O-^{16}O)$) and 841 cm^{-1} ($\nu(^{18}O-^{18}O)$; see Figure 3d, e, and f). The band of **1** at 965 cm^{-1}, which is isotope sensitive for both ^{13}C ($^{13}CO_2$) and ^{18}O ($H_2{}^{18}O_2$) substitutions, is attributed to the O–O–C(O)O moiety. It is also notable that there are two isotope-sensitive bands at 578 and 547 cm^{-1} in the ν(Fe–O) stretching-vibration region.

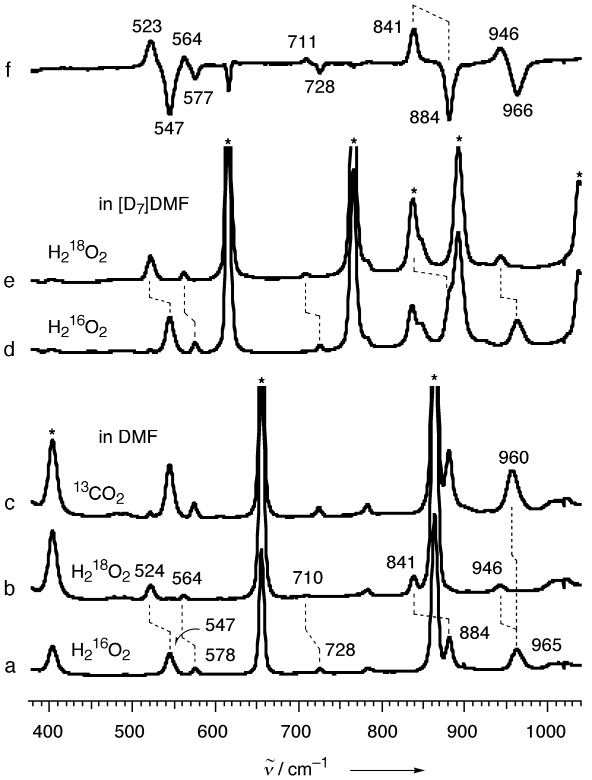

Figure 3. Resonance Raman spectra of **1** produced from $H_2{}^{16}O_2$ (a), $H_2{}^{18}O_2$ (b), $^{13}CO_2$ (c) in DMF at approximately -60 °C. Resonance Raman spectra of **1** produced in [D$_7$]DMF at approximately -60 °C from $H_2{}^{16}O_2$ (d) and $H_2{}^{18}O_2$ (e), and the difference spectrum (f) of the spectra (d) and (e) with 514.5 nm excitation. *: solvent bands.

In summary, we have succeeded for the first time in the structural characterization of a novel peroxocarbonate iron(III) complex (**1**) produced by the nucleophilic addition of a peroxide to CO_2. The peroxocarbonate ligand forms a five-membered chelate ring, which is responsible for the stabilization of the peroxocarbonate ligand. Compound **1** has an oxidation activity toward triphenylphosphane to triphenylphosphane oxide, but not toward olefins such as cyclohexene.

Experimental Section

1: A suspension of **2** (435 mg, 0.5 mmol) in DMF (30 mL) was dissolved by addition of DBU or $nBu_4N(OAc)$ (2 equivalents), and the resulting yellow solution was cooled to -60 °C. H_2O_2 (10 equivalents) was added to give a blue solution. A stream of CO_2 gas was passed over the blue solution at -60 °C for 30 min to afford a reddish yellow solution, to which Ph_4PBr (419 mg, 1 mmol) in methanol (30 mL) was added. The resulting solution was allowed to stand at -60 °C for a week to give orange crystals suitable for X-ray crystallography. Compound **1** was also prepared in a similar manner using acetonitrile as the solvent instead of DMF.

ESI mass spectra were obtained with an API 300 triple quadrupole mass spectrometer (PE-Sciex) in negative ion detection mode, equipped with an ion spray interface. A DMF solution produced by the reaction of **2** with H_2O_2, in the presence of DBU and CO_2 at -60 °C, was diluted with MeCN (1:19) and the resulting solution was introduced to the ionization source through a capillary, by the use of high Ar pressure at -40 °C.

Crystal data for **1**: triclinic, $P\bar{1}$, $a = 11.8188(5)$ Å, $b = 13.866(2)$, $c = 13.7010(9)$ Å, $\alpha = 83.806(3)$, $\beta = 86.610(4)$, $\gamma = 87.059(2)°$, $V = 2226.0(3)$ Å^3, $\rho_{calcd} = 1.343$ $g\,cm^{-3}$, $Z = 2$, $0.35 \times 0.20 \times 0.05$, $T = -160$ °C, $F_{000} = 936.00$, $\mu(Mo_{K\alpha}) = 4.36$ cm^{-1}, Rigaku Mercury CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71070$ Å), ω scans, 9240 measured, 6478 independent reflections ($I > 3.00\sigma(I)$), 556 parameters; structure solution with direct methods[14] and successive Fourier technique.[15] All non-hydrogen atoms of the complex anion and the counter ion, except for the disordered ones, were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions (0.95 Å). They were included, but not refined against $|F|$, to yield R (R_w) = 0.079 (0.116); largest residual electron densities 1.08/-0.81 near the iron atom (GOF = 2.03). CCDC-172141 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Helical Sense Bias Induced by Point Chirality in Cage Compounds**

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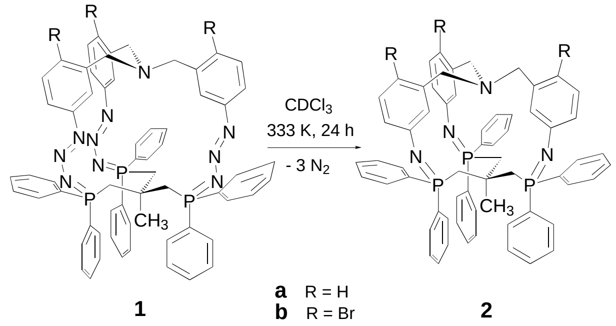
Dedicated to Professor José Elguero

At the molecular level, helical chirality[1] is usually a consequence of strong conformational preferences around covalent bonds. This is the case in molecular propellers, chiral molecules possessing two or more subunits which can be considered as "blades" (e.g., aryl or spirocyclic rings), which radiate from an axis of rotation (propeller axis).[2] Triarylmethanes are the most extensively studied structures of this class.[3] Bicyclic organic compounds of local C_3 symmetry, constructed by linking two propeller tripodal units exhibit this type of chirality. However, this propeller shape has been observed only for a limited number of such compounds in solution.[4] We have reported the preparation of several types of C_3 or pseudo-C_3 symmetric, chiral macrobicyclic triphosphazides (e.g. **1a**, Scheme 1), which possess propeller-like topology in solution and in the solid state.[5]



Scheme 1. Synthesis of **2** by dinitrogen expulsion from **1**.

Herein, we report that, when compound **1a** was kept at 333 K in $CDCl_3$ solution for 24 h, it cleanly converted into tri-λ^5-phosphazene **2a** in 75 % yield, by triple expulsion of molecular N_2 (Scheme 1). The dinitrogen expulsion from

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