

Dioxygenase Models. Crystal Structures of the 2,4-Pentanedionato, Phenanthrenesemiquinone, and Catecholato Complexes of *N,N'*-Ethylenebis(salicylideneaminato)iron(III)

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The X-ray structures of three complexes of $[\text{Fe}(\text{salen})]^+$ with bidentate ligands have been determined. $\text{Fe}(\text{salen})\text{acac}$ crystallizes in the orthorhombic space group $P2_12_12_1$ ($a = 8.568$ (6) Å, $b = 13.754$ (5) Å, $c = 18.330$ (7) Å, $\alpha = \beta = \gamma = 90.0^\circ$); $\text{Fe}(\text{salen})\text{PSQ}$, a chelated semiquinone complex, crystallizes in the monoclinic space group $P\bar{1}$ ($a = 9.997$ (2) Å, $b = 10.164$ (2) Å, $c = 13.368$ (2) Å, $\alpha = 94.41$ (2)°, $\beta = 105.67$ (2)°, $\gamma = 105.67$ (2)°); $\text{K}[\text{Fe}(\text{salen})\text{cat}]$, a chelated catecholate complex, crystallizes in the tetragonal space group $P4_2/mbc$ ($a = 23.187$ (9) Å, $b = 23.180$ (6) Å, $c = 26.937$ (7) Å, $\alpha = \beta = \gamma = 90.0^\circ$). In all three structures, the presence of the bidentate ligand forces the salen ligand to adopt the nonplanar *cis*- β configuration; all complexes exhibit distorted octahedral geometry, with the oxygen atoms of the bidentate ligand and an oxygen and a nitrogen atom from the salen defining the best equatorial plane. The remaining two ligating atoms are bent away from the bidentate ligand. The structural parameters obtained are in agreement with those found for similar complexes. $\text{Fe}(\text{salen})\text{PSQ}$ and $\text{K}[\text{Fe}(\text{salen})\text{cat}]$ represent structures modeling proposed species in the reaction mechanism of the catechol dioxygenases.

In our study of ferric phenolate and catecholate complexes^{1,2} as models for the catechol dioxygenases,³ we have investigated several $\text{Fe}(\text{saloph})\text{X}$ and $\text{Fe}(\text{salen})\text{X}$ complexes,⁴ where X is potentially a chelating or bridging ligand. We have reported the crystal structures of $\text{Fe}(\text{saloph})\text{catH}$ and $[\text{Fe}(\text{salen})]_2\text{hq}$.⁵ The former complex is a monodentate catecholate-iron complex, while the latter complex has a structure in which the hydroquinone bridges two $\text{Fe}(\text{salen})$ moieties. We report herein the crystal structures of three other $\text{Fe}(\text{salen})\text{X}$ complexes, where X is acetylacetonate, phenanthrenesemiquinone, and the catecholate dianion. All three complexes exhibit six-coordination, with the tetradentate salen ligand adopting a *cis*- β configuration⁶ in order to accommodate the bidentate ligand. The semiquinone and catecholate complexes are of particular interest because of the possible involvement of such species as intermediates in the mechanism of dioxygenase-catalyzed reactions.³

Experimental Section

Syntheses. **$\text{Fe}(\text{salen})\text{acac}$.** A 0.2-mL quantity (0.21 g, 2.0 mmol) of acetylacetonate was added to a refluxing solution of 0.50 g (1.3 mmol) of $\text{Fe}(\text{salen})\text{OAc}$ ⁷ in 50 mL of MeOH. The resulting red-orange solution was filtered and allowed to cool slowly. The dark purple plates were washed with MeOH. Yield: 0.34 g (62%) of $\text{Fe}(\text{salen})\text{acac} \cdot 0.7\text{MeOH}$. Anal. Calcd for $\text{C}_{21}\text{H}_{23.8}\text{FeN}_2\text{O}_{4.7}$: C, 58.74; H, 5.41; N, 6.31. Found: C, 58.93; H, 5.63; N, 6.27. During this investigation, another synthesis of $\text{Fe}(\text{salen})\text{acac}$ was reported.⁸ ¹H NMR (300 K, CDCl_3): δ -75 (sal H-3), 74 (sal H-4), -40 (sal H-5), 44 (sal H-6), 22 (acac Me).

$\text{Fe}(\text{salen})\text{PSQ}$. A THF solution of $\text{Fe}(\text{salen})\text{PSQ}$ was generated by the method of Floriani et al.⁹ Black plates of $\text{Fe}(\text{salen})\text{PSQ}$ were

Table I. Crystallographic Data

	$\text{Fe}(\text{salen})\text{acac}$	$\text{Fe}(\text{salen})\text{PSQ}$	$\text{K}[\text{Fe}(\text{salen})\text{cat}]$
formula	$\text{C}_{22}\text{H}_{25}\text{FeN}_2\text{O}_5$	$\text{C}_{30}\text{H}_{22}\text{FeN}_2\text{O}_4$	$\text{C}_{35}\text{H}_{44}\text{FeKN}_2\text{O}_{9.5}$
mol wt	453.30	530.42	739.69
space group	$P2_12_12_1$	$P\bar{1}$	$P4_2/mbc$
<i>a</i> , Å	8.568 (6)	9.997 (2)	23.187 (9)
<i>b</i> , Å	13.754 (5)	10.164 (2)	23.186 (6)
<i>c</i> , Å	18.330 (7)	13.368 (2)	26.937 (7)
α , deg	90.0	108.37 (1)	90.0
β , deg	90.0	94.41 (2)	90.0
γ , deg	90.0	105.67 (2)	90.0
<i>V</i> , Å ³	2160 (2)	1221.6 (4)	14 482 (8)
<i>Z</i>	4	2	16
<i>D</i> _{measd} , g/cm ³	1.400	1.448	1.34
<i>D</i> _{calcd} , g/cm ³	1.403	1.442	1.36
max (sin θ)/ λ	0.65	0.54	0.54
cryst size, mm	0.45 × 0.30 × 0.10	0.50 × 0.20 × 0.10	0.38 × 0.50 × 0.50
μ , cm ⁻¹	0.755	0.678	0.604
no. of reflns	2769	3193	3623
measd			
data used	2455	2854	2525
$[F \geq 3(\sigma(F))]$			
no. of variables used	347	401	439
<i>R</i>	0.074	0.048	0.133
<i>R</i> _w	0.102	0.072	0.186
goodness of fit ^a	0.293	0.238	0.298

$$^a \text{GOF} = [\sum w(F_o - kF_c)^2 / (N_{\text{obsd}} - N_v)]^{1/2}.$$

obtained by vapor diffusion of cyclohexane into the THF solution. **$\text{K}[\text{Fe}(\text{salen})\text{cat}]$.** $\text{K}[\text{Fe}(\text{salen})\text{cat}] \cdot 0.75(18\text{-crown-6}) \cdot \text{THF}$ was prepared according to published procedures.¹

Crystallographic Studies. Suitable crystals of the three compounds were cleaved to give parallelepipeds that were sealed in glass capillaries under nitrogen atmosphere. Preliminary oscillation and Weissenberg photographs revealed orthorhombic symmetry for $\text{Fe}(\text{salen})\text{acac}$, triclinic symmetry for $\text{Fe}(\text{salen})\text{PSQ}$, and tetragonal symmetry for $\text{K}[\text{Fe}(\text{salen})\text{cat}]$. Lattice constants were determined from least-squares fits of 15 moderate-angle diffractometer-measured reflections (Mo $K\alpha$ radiation; $\lambda = 0.71069$ Å) and are given in Table I. Complete sets of intensity data were collected on an automated four-circle Syntex $P2_1$ diffractometer using a variable-speed $1^\circ \omega$ scan and graphite-monochromated Mo $K\alpha$ radiation.

Refinement for $\text{Fe}(\text{salen})\text{acac}$ and $\text{Fe}(\text{salen})\text{PSQ}$. Systematic absences for $\text{Fe}(\text{salen})\text{acac}$ fitted the space group $P2_12_12_1$. $\text{Fe}(\text{salen})\text{PSQ}$ was assumed to belong to $P\bar{1}$ because density measurements showed two molecules per unit cell. Unsharpened Patterson synthesis gave the iron positions, and subsequent refinement and F_o syntheses

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- Abbreviations used: salen, *N,N'*-ethylenebis(salicylideneamine) dianion; saloph, *N,N'*-(1,2-phenylene)bis(salicylideneamine) dianion; catH₂, catechol; hqH₂, hydroquinone; acac, acetylacetonate; OAc, acetate; PSQ, phenanthrenesemiquinone; THF, tetrahydrofuran; bzac, benzoylacetonate; bzcz, 1,3-diphenyl-1,3-propanedionate.
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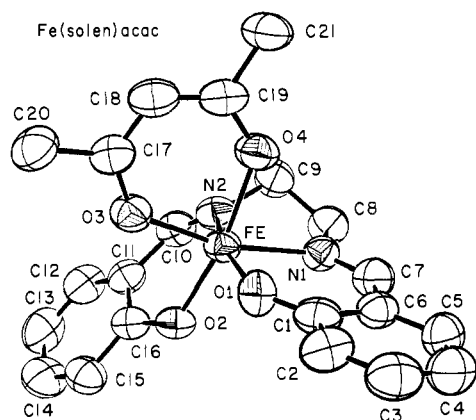


Figure 1. Structure and labeling of Fe(salen)acac. Thermal ellipsoids represent the 50% probability surfaces.

gave the positions of all remaining non-hydrogen atoms. After further refinement and compensation for anomalous scattering by iron, ΔF maps gave the positions of all hydrogen atoms. The hydrogen positions were refined with fixed isotropic temperature factors while anisotropic factors were used for all non-hydrogen atoms. All least-squares refinements were limited to diagonal elements until the final stages, when the matrices were blocked off as salicylyl and either acac or PSQ moieties. A weighting scheme using $1/\sigma_i$ was used in the refinements, and estimated standard deviations were obtained from BOND.¹⁰

Refinement for K[Fe(salen)cat]. Systematic absences for K[Fe(salen)cat]·0.75(18-crown-6)·THF uniquely fit $P4_2/mbc$. Since an unsharpened Patterson map was uninterpretable, an initial phasing model was obtained by a multisolution weighted tangent formula approach using the largest 292 E 's. A starting set of three special reflections generated 8 phase sets. A subsequent E -map calculation located the position of the iron atom.

Iterative block-diagonal refinements and F_o syntheses gave the positions of three potassium atoms (two at half-occupancy) and the remaining non-hydrogen atoms of the catecholate and salen ligands. The positions of two THF molecules and two 18-crown-6 molecules were also apparent. However, after several attempts at determining unique orientations for these four solvates, it was realized that each occupied two orientations, apparently dictated by the two half-occupied potassium positions. A rigid-body approach was rejected for the two 18-crown-6 molecules since their conformations were obviously altered by potassium coordination and no suitable models existed. All of the solvate THF molecules were located on a plane of symmetry such that a rigid-body fit would not have significantly reduced the number of parameters. Thus, two half-occupied positions were chosen for each of these molecules by fitting the F_o map with chemically sensible positions. These solvate molecules were refined with isotropic temperature factors. Hydrogen parameters were calculated but not refined for the iron complex with β 1.2 times the β of the attached carbon atom. A semiblocked (salicylyl, diimine-salicylyl, and catechol) matrix refinement converged at $R = 0.133$. A weighting scheme using $1/\sigma_i$ was used throughout the refinements, and estimated standard deviations were determined from BOND.¹⁰

Description of the Structures

Fe(salen)acac·MeOH crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$. The structure is shown in Figure 1 together with the numbering scheme for the molecule. Atomic coordinates and selected bond distances and bond angles are given in Tables II and III, respectively, while thermal parameters, the complete tables of bond lengths and bond angles, and structure factors are listed in Tables S-1, S-2,

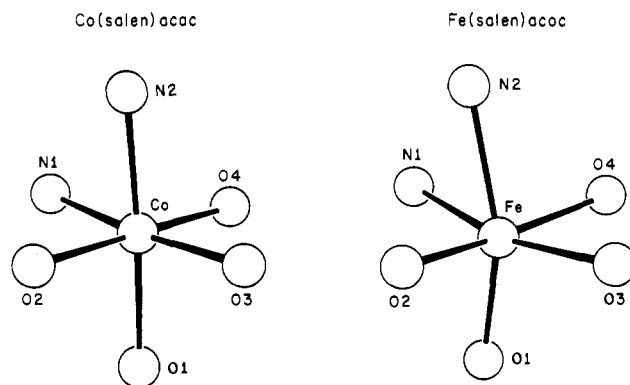


Figure 2. Comparison of the first coordination spheres of Co(salen)acac and Fe(salen)acac.

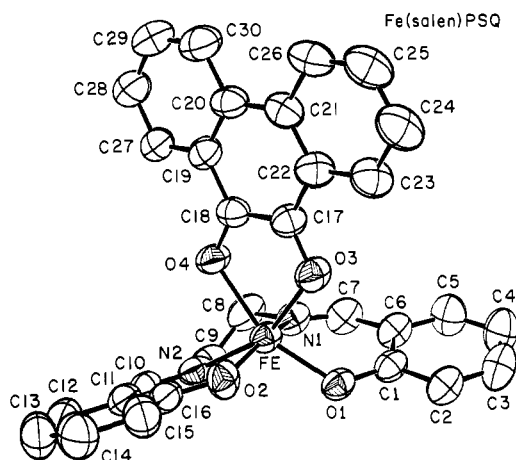


Figure 3. Structure and labeling of Fe(salen)PSQ. Thermal ellipsoids represent the 50% probability surfaces.

S-3, and S-4, respectively (supplementary material).

The complex is best described as a distorted octahedron with a structure similar to that of Co(salen)acac.¹¹ The best equatorial plane is defined by the acac oxygens and N1 and O2 of the salen ligand (average deviation 0.03 Å). The salen ligand adopts the nonplanar cis- β configuration⁶ to accommodate the bidentate ligand; this results in the rotation of a phenyl-imine nitrogen bond and the displacement of O2 by 1.75 Å from the plane defined by the iron and the other three ligating atoms in the salen. In this configuration, the interplanar angle between the two salicylidene rings is increased and the imine nitrogen is tetrahedrally distorted. This distortion is also reflected in the metal-ligand bond distances, where the "equatorial" Fe-N1 and Fe-O2 bond distances are about 0.05 Å longer than the corresponding "axial" bonds. The two Fe-O(acac) bonds also differ by 0.05 Å, with that trans to the nitrogen being shorter.

Figure 2 shows a comparison of the first coordination spheres of Fe(salen)acac and Co(salen)acac. The cobalt complex clearly approximates octahedral geometry more closely than does the iron complex, undoubtedly due to the large ligand field stabilization energy for low-spin Co(III). The high-spin ferric complex, lacking such stabilization, is more distorted from the ideal octahedron; this eases some of the strain imposed on the salen by the six-coordinate structure. To relieve some of the steric crowding, the "axial" N2-Fe-O1 angle shrinks while the "equatorial" N1-Fe-O2 angle increases. Bond lengths for the salen ligand, however, are comparable to those reported for other salen complexes.

(10) Computer programs used for the analyses were as follows: XRAY 76, the X-ray system of crystallographic programs (Stewart, J. M., Ed. Technical Report TR-445; University of Maryland: College Park, MD, March 1976); MULTAN 76, direct methods and fast Fourier transform (P. Main, University of York, York, England); ORTEP, crystallographic illustration program (Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN); BOND, structural parameters and errors (K. Hirotsu, Cornell University, 1978).

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Table II. Atomic Fractional Coordinates for Fe(salen)acac^a

atom	x	y	z
Fe	0.0357 (1)	0.0858 (0)	0.2065 (0)
O1	0.1120 (6)	-0.0390 (3)	0.1802 (3)
O2	-0.0773 (6)	0.1052 (3)	0.1148 (2)
O3	-0.1718 (6)	0.0515 (4)	0.2508 (2)
O4	0.1159 (7)	0.0784 (5)	0.3125 (2)
O5	-0.0520 (23)	-0.0441 (7)	0.0107 (4)
N1	0.2694 (7)	0.1362 (4)	0.1877 (3)
N2	0.0214 (8)	0.2379 (4)	0.2143 (3)
C1	0.2463 (10)	-0.0760 (5)	0.1636 (3)
C2	0.2596 (13)	-0.1762 (6)	0.1512 (4)
C3	0.3984 (16)	-0.2163 (7)	0.1320 (5)
C4	0.5320 (15)	-0.1630 (7)	0.1250 (5)
C5	0.5288 (12)	-0.0629 (7)	0.1384 (5)
C6	0.3849 (10)	-0.0185 (5)	0.1568 (3)
C7	0.3883 (10)	0.0835 (6)	0.1700 (4)
C8	0.2941 (10)	0.2412 (5)	0.1994 (4)
C9	0.1649 (11)	0.2789 (6)	0.2478 (5)
C10	-0.0782 (10)	0.2939 (5)	0.1854 (4)
C11	-0.2007 (9)	0.2607 (5)	0.1350 (3)
C12	-0.3113 (13)	0.3260 (7)	0.1123 (5)
C13	-0.4154 (12)	0.3053 (8)	0.0593 (6)
C14	-0.4028 (14)	0.2185 (9)	0.0242 (4)
C15	-0.2945 (11)	0.1500 (6)	0.0431 (4)
C16	-0.1863 (9)	0.1693 (5)	0.1001 (3)
C17	-0.2108 (10)	0.0392 (5)	0.3166 (3)
C18	-0.1170 (13)	0.0482 (7)	0.3752 (4)
C19	0.0406 (12)	0.0670 (5)	0.3719 (3)
C20	-0.3804 (12)	0.0150 (7)	0.3273 (4)
C21	0.1394 (13)	0.0755 (9)	0.4396 (4)
C22	-0.0672 (21)	-0.1347 (10)	0.0350 (6)
H2	0.166 (13)	-0.218 (8)	0.155 (5)
H3	0.381 (13)	-0.286 (8)	0.110 (5)
H4	0.661 (13)	-0.176 (8)	0.121 (5)
H5	0.615 (13)	-0.017 (8)	0.130 (5)
H7	0.473 (13)	0.129 (8)	0.163 (5)
H8-1	0.383 (13)	0.246 (8)	0.226 (5)
H8-2	0.277 (13)	0.270 (8)	0.151 (5)
H9-1	0.184 (13)	0.258 (8)	0.300 (5)
H9-2	0.128 (13)	0.317 (8)	0.255 (5)
H10	-0.097 (13)	0.278 (8)	0.143 (5)
H12	-0.320 (13)	0.351 (8)	0.131 (5)
H13	-0.501 (13)	0.327 (8)	0.060 (5)
H14	-0.464 (13)	0.218 (8)	-0.011 (5)
H15	-0.301 (13)	0.092 (8)	0.021 (5)
H18	-0.157 (13)	0.059 (8)	0.424 (5)
H20-1	-0.400 (14)	0.027 (8)	0.366 (6)
H20-2	-0.450 (14)	0.069 (8)	0.312 (6)
H20-3	-0.422 (14)	-0.051 (8)	0.315 (6)
H21-1	0.094 (14)	0.101 (8)	0.480 (6)
H21-2	0.215 (14)	0.012 (8)	0.456 (6)
H21-3	0.247 (14)	0.150 (8)	0.433 (6)
H22-1	-0.149 (17)	-0.158 (10)	0.021 (7)
H22-2	-0.015 (17)	-0.190 (10)	0.001 (7)
H22-3	-0.076 (17)	-0.153 (10)	0.084 (7)
H23	0.038 (20)	-0.003 (13)	0.053 (9)

^a Estimated standard deviations on the last significant digits are in parentheses.

By comparison to Fe(acac)₃,¹² the Fe(acac) interaction in this complex is somewhat weaker. The Fe–O bonds are somewhat longer (2.011 (5) and 2.063 (4) vs. 1.95 Å for Fe(acac)₃), and the bite angle is expectedly smaller (84.4 (2) vs. 90.0°). Other structural parameters for the acac, however, are comparable.

Fe(salen)PSQ crystallizes in the monoclinic space group *P*1̄, with a unit cell consisting of two pseudooctahedral molecules related by a center of inversion. The structure and the numbering scheme for the molecule are shown in Figure 3. Selected structural parameters and atomic coordinates are given in Tables III and IV, respectively, while thermal parameters, the complete tables of bond lengths and bond angles, and

structure factors can be found in Tables S-5, S-6, S-7, and S-8, respectively (supplementary material).

As in Fe(salen)acac, the complex is a distorted octahedron, with the PSQ oxygens and O1 and N2 of the salen ligand defining the best equatorial plane (average deviation 0.11 Å). The PSQ is chelated to the iron, resulting in the displacement of the O1 oxygen of the salen 1.53 Å out of the plane defined by the iron and the other three ligating atoms of salen. The “equatorial” Fe–N2 bond is longer than the corresponding “axial” bond, and the Fe–O(PSQ) bond trans to the “equatorial” nitrogen is shorter than the other Fe–O(PSQ) bond. Interestingly, the Fe–O(salen) bonds do not appear to be different. By comparison to Fe(PSQ)₃,¹³ the Fe(PSQ) interaction in Fe(salen)PSQ is slightly weaker; the Fe–O bonds are longer (2.047 (3) and 2.099 (3) vs. 2.027 Å for Fe(PSQ)₃), and the bite angle is somewhat smaller (76.5 (1) vs. 79.4°). The structural parameters for the salen and PSQ ligands are unexceptional.

Earlier magnetic and Mössbauer studies¹⁴ of this complex and related species have described these complexes as *S* = 2 systems resulting from the antiferromagnetic coupling ($-J > 600 \text{ cm}^{-1}$) of a high-spin ferric center with a coordinated semiquinone radical anion. Our structural results confirm these conclusions. The metal–ligand bond distances agree well with those of other high-spin ferric complexes, and the C–O and C–C bond distances of the bidentate ligand are consistent with the semiquinone formulation. Fe(salen)PSQ also exhibits the stacking of PSQ units in the unit cell observed in a number of PSQ complexes;¹⁵ it has been suggested that this gives rise to the intermolecular antiferromagnetic interactions observed for many of these complexes. The interplanar spacing for Fe(salen)PSQ is 3.57 Å, which is somewhat longer than the spacing (3.35 Å) observed in Fe(PSQ)₃PSQ; the intermolecular interactions nevertheless appear to persist even at this distance.

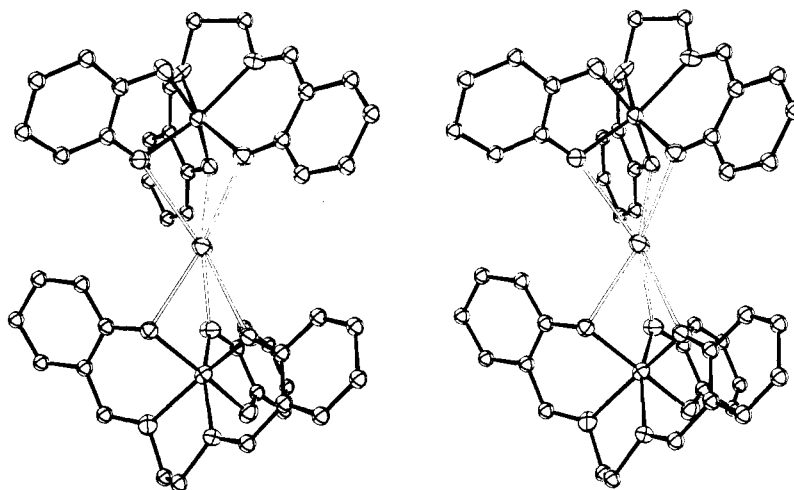
K[Fe(salen)cat] crystallizes out of THF solution in the presence of 18-crown-6 in the tetragonal space group *P*4₂/*mbc*. The unit cell consists of a cationic aggregate, an anionic aggregate, and a solvent molecule in eight special positions. A stereoview of the anionic aggregate, K[Fe(salen)cat]₂⁻, is shown in Figure 4. The structure of the anionic complex with the corresponding numbering scheme is shown in Figure 5. Atomic coordinates for the iron complex and selected structural parameters are given in Tables V and III, respectively; atomic coordinates for the remaining unit cell contents, thermal parameters, complete lists of bond lengths and bond angles, and structure factors can be found in Tables S-9, S-10, S-11, S-12, and S-13, respectively (supplementary material).

The potassium cation is found in three noncrystallographically related positions, one being in the anionic aggregate. This potassium is situated with full occupancy in a trigonal prism of oxygen atoms (Figure 4) derived from two [Fe(salen)cat]⁻ moieties, with the O1, O2, and O4 atoms from each complex forming a trigonal face in the potassium coordination sphere. Such interactions have been documented previously for both salen^{16–19} and catecholate^{20,21} complexes.

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Table III. Selected Structural Parameters

Fe(salen)acac				Bond Angles (Deg)			
Bond Distances (Å)				O1-Fe-O2	97.0 (1)	O4-Fe-N2	81.1 (1)
Fe-O1	1.899 (4)	N1-C8	1.476 (9)	O1-Fe-O3	85.1 (1)	N1-Fe-N2	76.0 (1)
Fe-O2	1.958 (4)	N2-C9	1.485 (11)	O1-Fe-O4	156.9 (1)	Fe-O1-C1	125.4 (2)
Fe-O3	2.011 (5)	N2-C10	1.265 (10)	O1-Fe-N1	83.8 (1)	Fe-O2-C16	133.7 (3)
Fe-O4	2.063 (4)	C6-C7	1.424 (11)	O1-Fe-N2	116.9 (1)	Fe-O3-C17	116.5 (3)
Fe-N1	2.146 (6)	C8-C9	1.510 (12)	O2-Fe-O3	97.6 (1)	Fe-O4-C18	114.3 (3)
Fe-N2	2.100 (6)	C10-C11	1.472 (11)	O2-Fe-O4	99.1 (1)	Fe-N1-C7	125.5 (4)
O1-C1	1.294 (10)	C11-C16	1.415 (9)	O2-Fe-N1	158.7 (1)	Fe-N1-C8	114.0 (3)
O2-C16	1.313 (9)	C17-C18	1.348 (11)	O2-Fe-N2	84.9 (1)	C7-N1-C8	120.4 (5)
O3-C17	1.262 (7)	C17-C20	1.503 (13)	O3-Fe-O4	76.5 (1)	Fe-N2-C9	114.3 (3)
O4-C19	1.275 (8)	C18-C19	1.377 (15)	O3-Fe-N1	103.7 (1)	Fe-N2-C10	125.6 (3)
N1-C7	1.291 (10)	C19-C21	1.507 (11)	O3-Fe-N2	157.5 (1)	C9-N2-C10	119.4 (4)
				O4-Fe-N1	87.1 (1)		
Bond Angles (Deg)				K[Fe(salen)cat]			
O1-Fe-O2	94.3 (2)	O4-Fe-N2	90.3 (2)	Bond Distances (Å)			
O1-Fe-O3	101.2 (2)	N1-Fe-N2	75.2 (2)	Fe-O1	1.994 (9)	N2-C10	1.263 (22)
O1-Fe-O4	94.6 (3)	Fe-O1-C1	136.1 (5)	Fe-O2	1.988 (9)	C1-C6	1.400 (21)
O1-Fe-N1	86.0 (2)	Fe-O2-C16	128.3 (4)	Fe-O3	1.988 (9)	C6-C7	1.393 (23)
O1-Fe-N2	159.7 (2)	Fe-O3-C17	130.6 (5)	Fe-O4	1.989 (9)	C8-C9	1.470 (24)
O2-Fe-O3	86.6 (2)	Fe-O4-C19	129.9 (6)	Fe-N1	2.131 (12)	C10-C11	1.437 (26)
O2-Fe-O4	168.4 (2)	Fe-N1-C7	126.5 (5)	Fe-N2	2.184 (13)	C11-C16	1.393 (24)
O2-Fe-N1	106.2 (2)	Fe-N1-C8	115.3 (5)	O1-C1	1.327 (17)	C17-C18	1.411 (20)
O2-Fe-N2	83.9 (2)	C7-N1-C8	118.2 (7)	O2-C16	1.309 (19)	C17-C22	1.360 (22)
O3-Fe-O4	84.4 (2)	Fe-N2-C9	110.9 (5)	O3-C17	1.310 (18)	C18-C19	1.355 (23)
O3-Fe-N1	164.9 (2)	Fe-N2-C10	128.1 (5)	O4-C18	1.338 (16)	C19-C20	1.379 (30)
O3-Fe-N2	98.9 (2)	C9-N2-C10	120.0 (6)	N1-C7	1.286 (21)	C20-C21	1.416 (39)
O4-Fe-N1	81.8 (2)			N1-C8	1.486 (23)	C21-C22	1.417 (27)
				N2-C9	1.506 (21)		
Fe(salen)PSQ				Bond Angles (Deg)			
Bond Distances (Å)				O1-Fe-O2	90.4 (4)	O4-Fe-N2	165.3 (4)
Fe-O1	1.919 (3)	N2-C10	1.262 (5)	O1-Fe-O3	162.3 (4)	N1-Fe-N2	75.3 (5)
Fe-O2	1.913 (3)	C1-C6	1.415 (6)	O1-Fe-O4	84.9 (4)	Fe-O1-C1	130.0 (8)
Fe-O3	2.047 (3)	C6-C7	1.443 (8)	O1-Fe-N1	82.8 (5)	Fe-O2-C16	131.0 (9)
Fe-O4	2.099 (3)	C8-C9	1.507 (7)	O1-Fe-N2	109.9 (4)	Fe-O3-C17	114.1 (9)
Fe-N1	2.111 (4)	C10-C11	1.445 (7)	O2-Fe-O3	101.9 (4)	Fe-O4-C18	111.7 (8)
Fe-N2	2.160 (3)	C11-C16	1.423 (6)	O2-Fe-O4	96.0 (4)	Fe-N1-C7	127.3 (11)
O1-C1	1.330 (5)	C17-C18	1.429 (6)	O2-Fe-N1	154.6 (5)	Fe-N1-C8	108.4 (10)
O2-C16	1.314 (5)	C17-C22	1.434 (5)	O2-Fe-N2	84.2 (5)	C7-N1-C8	123.4 (13)
O3-C17	1.281 (4)	C18-C19	1.439 (5)	O3-Fe-O4	81.3 (4)	Fe-N2-C9	113.8 (9)
O4-C18	1.282 (4)	C19-C20	1.410 (6)	O3-Fe-N1	90.9 (5)	Fe-N2-C10	127.0 (11)
N1-C7	1.269 (7)	C20-C21	1.458 (7)	O3-Fe-N2	84.3 (4)	C9-N2-C10	118.2 (14)
N1-C8	1.469 (8)	C21-C22	1.413 (5)	O4-Fe-N1	107.6 (5)		
N2-C9	1.481 (7)						

Figure 4. Stereoview of the $K[Fe(salen)cat]_2^-$ aggregate.

The $[Fe(salen)cat]^-$ complex adopts an octahedral structure with distortions similar to those of the two structures described earlier. Again, the best equatorial plane (average deviation 0.10 Å) is defined by the oxygens of the bidentate ligand and the O1 and N2 of the salen ligand. For accommodation of the bidentate ligand, the O1 atom of the salen is displaced 1.63 Å from the plane defined by Fe, O2, N1, and N2. As with $Fe(salen)acac$ and $Fe(salen)PSQ$, the "axial" Fe-N1 bond is

shorter than the "equatorial" Fe-N2 bond by 0.05 Å; however, the Fe-O bonds of the bidentate ligand are essentially of the same length in this complex, in contrast to those of the other two complexes. The Fe-O4 bond, which is trans to the equatorial nitrogen and thus expected to be shorter than Fe-O3, is probably lengthened because of the additional potassium interaction. The iron atom appears somewhat larger in this complex than in the other two, possibly as a result of the

Table IV. Atomic Fractional Coordinates for Fe(salen)PSQ

atom	x	y	z
Fe	0.2395 (0)	0.2076 (0)	0.1219 (0)
O1	0.3006 (3)	0.0938 (2)	0.0009 (2)
O2	0.1886 (3)	0.0616 (3)	0.1862 (2)
O3	0.4491 (3)	0.2915 (3)	0.1892 (2)
O4	0.2490 (3)	0.3914 (3)	0.2537 (2)
N1	0.2164 (4)	0.3308 (3)	0.0245 (3)
N2	0.0179 (3)	0.1895 (3)	0.1049 (2)
C1	0.3913 (4)	0.1475 (4)	-0.0549 (3)
C2	0.4832 (5)	0.0733 (5)	-0.0985 (3)
C3	0.5781 (6)	0.1264 (6)	-0.1563 (4)
C4	0.5826 (7)	0.2524 (7)	-0.1770 (4)
C5	0.4881 (6)	0.3235 (6)	-0.1388 (4)
C6	0.3932 (5)	0.2750 (4)	-0.0772 (3)
C7	0.2895 (6)	0.3479 (5)	-0.0466 (4)
C8	0.0981 (6)	0.3907 (5)	0.0398 (4)
C9	-0.0260 (6)	0.2648 (5)	0.0359 (4)
C10	-0.0675 (4)	0.1392 (5)	0.1584 (3)
C11	-0.0416 (4)	0.0603 (4)	0.2270 (3)
C12	-0.1469 (6)	0.0136 (6)	0.2819 (4)
C13	-0.1351 (6)	-0.0680 (7)	0.3431 (4)
C14	-0.0136 (7)	-0.1094 (7)	0.3488 (4)
C15	0.0940 (6)	-0.0668 (5)	0.2953 (4)
C16	0.0838 (4)	0.0206 (4)	0.2345 (3)
C17	0.4842 (4)	0.4046 (4)	0.2746 (3)
C18	0.3732 (4)	0.4620 (4)	0.3090 (3)
C19	0.4047 (4)	0.5960 (4)	0.3986 (3)
C20	0.5435 (5)	0.6627 (4)	0.4571 (3)
C21	0.6543 (4)	0.5976 (4)	0.4268 (3)
C22	0.6254 (4)	0.4719 (4)	0.3342 (3)
C23	0.7330 (5)	0.4136 (5)	0.3011 (4)
C24	0.8687 (5)	0.4747 (6)	0.3591 (5)
C25	0.8962 (5)	0.5945 (6)	0.4512 (4)
C26	0.7935 (5)	0.6568 (5)	0.4860 (4)
C27	0.2988 (5)	0.6604 (5)	0.4247 (3)
C28	0.3280 (6)	0.7891 (6)	0.5079 (4)
C29	0.4623 (7)	0.8543 (6)	0.5661 (5)
C30	0.5684 (6)	0.7936 (6)	0.5436 (4)
H2	0.486 (6)	-0.006 (6)	-0.085 (4)
H3	0.644 (7)	0.085 (7)	-0.178 (5)
H4	0.653 (7)	0.283 (7)	-0.217 (5)
H5	0.492 (6)	0.411 (6)	-0.159 (5)
H7	0.279 (6)	0.398 (6)	-0.088 (4)
H81	0.082 (6)	0.421 (6)	-0.030 (4)
H82	0.118 (6)	0.468 (6)	0.114 (5)
H91	-0.056 (6)	0.197 (6)	-0.042 (5)
H92	-0.100 (6)	0.290 (6)	0.057 (5)
H10	-0.158 (6)	0.147 (5)	0.144 (4)
H12	-0.230 (7)	0.035 (6)	0.272 (5)
H13	-0.209 (7)	-0.101 (7)	0.388 (5)
H14	-0.005 (7)	-0.155 (7)	0.394 (5)
H15	0.178 (6)	-0.089 (6)	0.304 (4)
H23	0.705 (6)	0.333 (6)	0.238 (5)
H24	0.942 (7)	0.438 (7)	0.336 (5)
H25	0.991 (7)	0.639 (7)	0.500 (5)
H26	0.815 (6)	0.745 (7)	0.545 (5)
H27	0.210 (6)	0.614 (6)	0.386 (4)
H28	0.254 (7)	0.830 (7)	0.514 (5)
H29	0.476 (7)	0.936 (7)	0.622 (5)
H30	0.659 (6)	0.833 (6)	0.589 (4)

negative charge on the complex. The salen and cat structural parameters, however, compare favorably with those of other salen and cat complexes.

The remaining components of this unit cell are disordered, resulting in a greater uncertainty of the parameters obtained for this structure. The cationic aggregate consists of THF·K_a·18-crown-6·K_b·0.5(18-crown-6). The two crown ether moieties lie in perpendicular planes, with the latter also bisected by a twofold axis. The two potassium positions are filled at half-occupancy with both K_a and K_b above or below the mean plane of the first crown ether. K_a is then capped with THF, while K_b is capped with an oxygen from the latter crown ether. Finally, another molecule of THF is found, which is not associated with either aggregate; this is also disordered. The

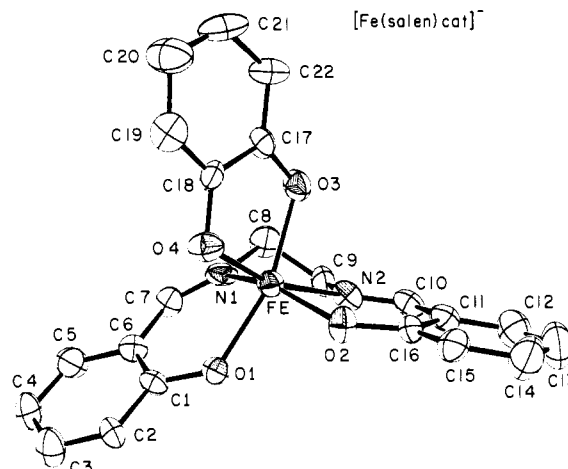


Figure 5. Structure and labeling of [Fe(salen)cat]⁻. Thermal ellipsoids represent the 25% probability surfaces.

Table V. Atomic Fractional Coordinates for the K[Fe(salen)cat]₂⁻ Aggregate

atom	x	y	z
Fe	0.8345 (0)	0.1252 (0)	0.2435 (0)
O1	0.8187 (4)	0.1903 (4)	0.1970 (3)
O2	0.7508 (4)	0.1070 (4)	0.2465 (4)
O3	0.8654 (5)	0.0787 (4)	0.2995 (3)
O4	0.8332 (4)	0.1855 (4)	0.2959 (3)
N1	0.9174 (5)	0.1275 (6)	0.2093 (5)
N2	0.8402 (6)	0.0444 (6)	0.2021 (4)
C1	0.8532 (6)	0.2322 (6)	0.1815 (5)
C2	0.8321 (8)	0.2832 (7)	0.1674 (7)
C3	0.8648 (9)	0.3268 (8)	0.1506 (10)
C4	0.9260 (10)	0.3194 (9)	0.1443 (8)
C5	0.9471 (8)	0.2663 (10)	0.1582 (8)
C6	0.9123 (7)	0.2217 (7)	0.1755 (5)
C7	0.9403 (6)	0.1699 (7)	0.1857 (6)
C8	0.9409 (7)	0.0679 (8)	0.2084 (7)
C9	0.8991 (7)	0.0328 (6)	0.1807 (7)
C10	0.8033 (8)	0.0043 (7)	0.2010 (6)
C11	0.7457 (8)	0.0078 (8)	0.2204 (6)
C12	0.7108 (12)	-0.0394 (9)	0.2129 (8)
C13	0.6552 (16)	-0.0397 (12)	0.2295 (12)
C14	0.6316 (10)	0.0108 (12)	0.2500 (10)
C15	0.6670 (8)	0.0564 (7)	0.2572 (6)
C16	0.7231 (7)	0.0583 (7)	0.2405 (6)
C17	0.8721 (7)	0.1077 (6)	0.3408 (6)
C18	0.8541 (6)	0.1657 (6)	0.3390 (5)
C19	0.8609 (7)	0.1984 (7)	0.3803 (7)
C20	0.8842 (13)	0.1818 (11)	0.4252 (8)
C21	0.9020 (10)	0.1234 (13)	0.4248 (6)
C22	0.8940 (7)	0.0860 (8)	0.3838 (5)
K1	0.7283 (1)	1.2283 (0)	0.2500 (0)

stoichiometry of the complex is thus found to be K[Fe(salen)cat]·0.75(18-crown-6)·THF, with the elemental analysis and GC quantitation of the crown ether and THF contents.

Discussion

We have reported the crystal structures of three Fe(salen)L complexes, where L is a bidentate ligand. In all cases, the salen distorts to the nonplanar cis-β configuration⁶ to accommodate the coordination of the bidentate ligand. This distortion requires the rotation of the phenyl-imine nitrogen bond such that the interplanar angle of the two salicylidene moieties increases; at the same time, the imine nitrogen becomes tetrahedrally distorted. Similar structural changes are observed for Co(salen)acac,¹¹ Co(salen)bzac,²² and Co(saloph)bzcz.²³

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Table VI. Bond Angles (Deg) for Various salen Complexes

complex	imine torsional angles	sal-sal interplanar angle	salen N-M-O angles	
			"axial"	"equatorial"
[Fe(salen)] ₂ hq ^a	179, 177	8.4	144	154
Fe(salen)PSQ ^b	178, 171	28.1	159	117
[Fe(salen)cat] ^{-b}	179, 163	39.8	155	110
Fe(salen)acac ^b	180, 163	52.6	160	106
Co(salen)acac ^c	180, 153	58.6	176	97

^a Reference 5. ^b This work. ^c Reference 11.

Table VI shows a comparison of the distortions observed for the three iron complexes and a cobalt complex relative to an undistorted five-coordinate iron complex. The interplanar angle increases from 8.4° in [Fe(salen)]₂hq to 58.6° for Co(salen)acac, while the imine torsional angle decreases from 177° in the five-coordinate complex to 153° in the near-octahedral cobalt complex. It is clear that the cobalt complex shows the largest distortions, and this is a result of the greater preference of Co(III) for an octahedral environment. The iron complexes exhibit varying degrees of distortion toward the cis-β configuration depending on the bidentate ligand.

We have obtained the structures of these complexes because of our interest in dioxygenase models and iron-phenolate interactions. The structures of the PSQ and catecholate complexes are relevant to our understanding of the catechol dioxygenases; they serve as models for proposed species in the dioxygenase mechanism.³ The question as to whether the substrate is chelated to the metal center in the enzyme has been amply discussed, and evidence for both monodentate and bidentate coordination modes has been presented.^{2,3,24-26} We have recently reported the structure of Fe(saloph)catH,⁵ a complex with monodentate catecholate coordination; [Fe(salen)cat]⁻ affords the same ligating groups, but with the catecholate chelated to the iron. Studies on the reactivity of these complexes toward dioxygen show that the monodentate catecholate complex reacts readily to form Fe(salen)DBSQ, while the chelated complex is unreactive.² This provides further support for a monodentate catecholate interaction in the catechol dioxygenases.

The Fe(salen)PSQ complex is a model for the species proposed as the first intermediate in the reaction of the ES complex with O₂,³ in the proposed mechanism, the coordinated catecholate reduces dioxygen to generate a ferric semiquinone

complex. The magnetic properties of Fe(salen)PSQ and analogous complexes have been characterized, and they are best described as *S* = 2 systems resulting from antiferromagnetic coupling between high-spin ferric centers with semiquinone ligands.¹⁴ The crystal structure of Fe(salen)PSQ is consistent with this, as is our recently reported NMR data.²

The structures are also relevant to our understanding of iron-phenolate interactions. Studies of the NMR spectra of a series of Fe(salen)L complexes show that the contact shifts for the salicylidene protons dramatically decrease in going from the monodentate catecholate coordination in Fe(salen)catH to the chelated form in [Fe(salen)cat]⁻.¹ The H-3 and H-4 resonances on the salen ligand are separated by about 140 ppm in the former complex but only by 100 ppm in the latter. We thought that the decrease in the shifts could perhaps be due to the structural change to a six-coordinate species. The NMR spectra of Fe(salen)acac and Fe(salen)DBSQ, which exhibit spans of 150 and 115 ppm, respectively, clearly show that the presence of a bidentate ligand does not necessarily result in a dramatic decrease in the contact shifts. Instead, we have found that the NMR spectral changes observed are related to the energy of the phenolate-to-iron charge-transfer interaction.²⁷

In conclusion, we have reported the structures of three Fe(salen)L complexes, where L is a bidentate ligand. Knowledge of these structures should contribute to our understanding of the active-site structure and mechanism of the catechol dioxygenases and iron-phenolate interactions in general.

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Registry No. Fe(salen)acac-0.7MeOH, 83463-18-7; Fe(salen)PSQ, 83509-93-7; K[Fe(salen)cat]·0.75(18-crown-6)·THF, 83509-95-9.

Supplementary Material Available: Tables S-1-S-4 listing thermal parameters, bond lengths, bond angles, and structure factors, respectively, for Fe(salen)acac, Tables S-5-S-8 listing thermal parameters, bond lengths, bond angles, and structure factors, respectively, for Fe(salen)PSQ, and Tables S-9-S-13 listing the atomic coordinates for the cation and solvates, thermal parameters, bond lengths, bond angles, and structure factors, respectively, for K[Fe(salen)cat] (48 pages). Ordering information is given on any current masthead page.

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