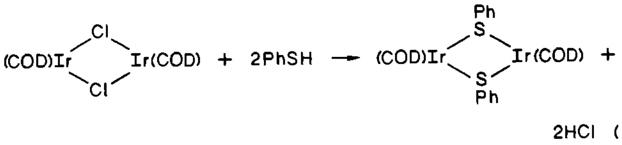
be produced by the action of small amounts of benzenethiol generated in solution by decomposition of diphenyl disulfide also (eq 4). It is interesting that in reaction 3 not only does oxidative addition occur but also migration of the preferred bridging ligands, PhS, occurs concomitantly.



(4)

Acknowledgment. We are grateful to the National Science Foundation for support at Texas A&M and the CAICYT (Project No. 3275/83) for support in Valencia.

Registry No. **1**, 63312-26-5; **2**, 114466-63-6; **3**, 114466-64-7; **4**, 114490-26-5; $Ir_2(OMe)_2(COD)_2$, 12148-71-9; $Ir_2Cl_2(COD)_2$, 12112-67-3; PhSSPh, 882-33-7; $Ir_2(\mu\text{-}I)_2I_2(COD)_2$, 101224-47-9; $Ir(\mu\text{-}Br)_2Br_2(COD)_2$, 12245-73-7.

Supplementary Material Available: Tables of bond distances, bond angles, and general displacement parameters for both compounds (10 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische und Analytische Chemie,
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Tris((trifluoromethyl)sulfonyl)methane, $HC(SO_2CF_3)_3$

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Tris((trifluoromethyl)sulfonyl)methane, $HC(SO_2CF_3)_3$, is prepared from CH_3MgBr and CF_3SO_2F. Known $H_2C(SO_2CF_3)_2$ is an intermediate. This novel material is a very strong C–H acid. Some derivatives, such as salts and halogen compounds, are described. The crystal structure of $K^+C(SO_2CF_3)_3^-\cdot H_2O$ is presented. Crystal data: $a = 605.91$ (6) pm, $b = 1398.77$ (8) pm, $c = 1605.60$ (13) pm, $Pc2_1b$, $Z = 4$.

Introduction

In search of extremely electronegative groups having carbon as the central atom we sought a way of preparing $CH(SO_2CF_3)_3$. One motive for this search was the potential for forming a stable xenon–carbon bond. Many other carbon ligands, such as $C(CN)_3$, $C(NO_2)_3$, CN, C_6F_5, or $C(SO_2F)_3$,[1] have failed to do this. The only unconfirmed report of macroscopic amounts of a Xe–C-bonded species is that of $Xe(CF_3)_2$,[2] which is supposed to be thermally quite unstable.

The success of preparing xenon–nitrogen bonds, first with the $N(SO_2F)_2$ ligand[3] and later and better with the $N(SO_2CF_3)_2$ ligand,[4] suggested $C(SO_2CF_3)_3$ as a possible candidate for a Xe–C-bonded ligand, even though $C(SO_2F)_3$ had failed to give a xenon–carbon bonded species.[5]

Results and Discussion

Our first attempts to prepare $HC(SO_2CF_3)_3$ were unsuccessful. Thus we have not been able to obtain the title compound by transfer of trifluoromethyl groups onto $HC(SO_2OH)_3$ or $HC(SO_2F)_3$.[5] We were also unable to oxidize the known $HC(SCF_3)_3$ molecule.[6] These negative findings led to the trifluoromethyl sulfonation of $CH_2(SO_2CF_3)_2$ or, in other words, stepwise trifluoromethyl sulfonation of methane. $CH_2(SO_2CF_3)_2$ is prepared from CH_3MgBr and CF_3SO_2F and is itself a quite strong CH acid.[7] In fact, with CH_3MgBr, 2 mol of CH_4 are formed, an indication of the existence of the $C(SO_2CF_3)_2^{2-}$ dianion in solution.[7] This dianion is reacted with CF_3SO_2F to give $C(SO_2CF_3)_3^-$ from which the title compound can be isolated. It is possible to circumvent the isolation of $CH_2(SO_2CF_3)_2$ by reacting CH_3MgBr and CF_3SO_2F in the appropriate ratio.

Table I. Atomic Coordinates of $K^+C(SO_2CF_3)_3^-\cdot H_2O$ (Except for Hydrogen Atoms)

	x	*y*	*z*
K	0.948 (4)	0.51710 (0)	0.39040 (8)
O	0.429 (2)	0.5388 (5)	0.8584 (4)
S1	0.1031 (3)	0.2433 (2)	0.46323 (7)
S2	0.0297 (2)	0.0645 (2)	0.36421 (7)
S3	0.1196 (2)	0.2502 (2)	0.28040 (7)
O1	0.0559 (8)	0.1789 (3)	0.5294 (3)
O11	−0.0002 (8)	0.3353 (3)	0.4610 (3)
O3	0.2030 (7)	0.1933 (4)	0.2138 (2)
O31	0.2246 (7)	0.3390 (3)	0.3020 (3)
O2	−0.0311 (7)	0.0393 (3)	0.2807 (2)
O21	−0.1008 (7)	0.0310 (3)	0.4325 (3)
C	0.0802 (9)	0.1840 (4)	0.3696 (3)
C1	0.407 (2)	0.2716 (5)	0.4768 (4)
F11	0.4428 (8)	0.3620 (3)	0.4648 (3)
F12	0.4654 (7)	0.2458 (4)	0.5522 (3)
F13	0.5276 (6)	0.2227 (4)	0.4242 (3)
C2	0.299 (1)	0.0067 (5)	0.3801 (4)
F21	0.3765 (6)	0.0289 (3)	0.4554 (2)
F22	0.4431 (6)	0.0365 (4)	0.3245 (3)
F23	0.2788 (7)	−0.0871 (3)	0.3760 (3)
C3	−0.1589 (9)	0.2874 (5)	0.2468 (4)
F31	−0.2435 (6)	0.3503 (4)	0.2996 (3)
F32	−0.2915 (6)	0.2143 (3)	0.2401 (3)
F33	−0.1444 (7)	0.3300 (3)	−0.1733 (2)

Table II. Selected Bond Distances in $K^+C(SO_2CF_3)_3^-\cdot H_2O$ (pm)[a]

C–S	169.3, 172.6, 172.7
S–O	143.0, 142.8, 143.5, 143.5, 143.7, 143.2
S–C(F)	189.5, 184.7, 184.2
C–F	130.1, 133.6
K···O(S)	257.9, 284.5, 284.8, 287.0, 297.6, 305.0
K···O(H)	294.7, 322.9
K···F(C)	325.3, 343.3, 378.3

[a] Estimated standard deviations 0.3–0.8 ppm.

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0020-1669/88/1327-2135$01.50/0

$$CH_2(SO_2CF_3)_2 \xrightarrow[-2CH_4]{2CH_3MgBr} (MgBr^+)_2C(SO_2CF_3)_2{}^{2-} \xrightarrow[-MgBrF]{CF_3SO_2F}$$

$$MgBr^+C(SO_2CF_3)_3{}^- \xrightarrow[-BrMgHSO_4]{+H_2SO_4} HC(SO_2CF_3)_3$$

$$\begin{aligned} &4CH_3MgBr + 3CF_3SO_2F \longrightarrow \\ &\qquad MgBr^+C(SO_2CF_3)_3{}^- + 3CH_4 + 3MgBrF \\ &\qquad \Big\downarrow H_2SO_4 \\ &\qquad HC(SO_2CF_3)_3 + BrMgHSO_4 \end{aligned}$$

Tris((trifluoromethyl)sulfonyl)methane is a very strong acid in aqueous solution, from which alkali-metal and silver salts can be isolated. No reliable means of determining its acid strength were available to us. The acid strength of $HC(SO_2F)_3$, however, has been estimated by means of Raman spectroscopy to lie between those of concentrated HNO_3 and $HOSO_2F$.[5] We assume a similar value for the title compound.

The cesium salt is surprisingly insoluble in water. Crystals of it are rhombohedral but of very poor quality. The potassium salt forms orthorhombic crystals of good quality. The results from the crystal structure analysis of $K^+C(SO_2CF_3)_3{}^-\cdot H_2O$ are shown in Tables I–III and Figure 1. Not surprisingly, the CS_3 skeleton of the anion is planar, as was found for the $C(SO_2F)_3{}^-$ anion.[5] Another similarity is the unsymmetric orientation of the CF_3 groups: two CF_3 groups are located below and one is located above the CS_3 plane, as are the F atoms in $C(SO_2F)_3{}^-$. The K^+ ion is surrounded by seven oxygen atoms in a very irregular manner, with contact distances of up to 305 ppm. Six of these oxygens are sulfur oxygens; the seventh is the water oxygen. Contacts to the fluorine atoms and to another water molecule have distances of more than 322 ppm.

The silver salt was used for the preparation of the halogen derivatives $ClC(SO_2CF_3)_3$ and $BrC(SO_2CF_3)_3$:

$$Ag^+C(SO_2CF_3)_3{}^- + X_2 \rightarrow AgX + X\text{–}C(SO_2CF_3)_3$$
$$X = Cl, Br$$

The chloro derivative is an oxidant as can be seen from its reaction with I^-:

$$Cl\text{–}C(SO_2CF_3)_3 + 2I^- \rightarrow C(SO_2CF_3)_3{}^- + Cl^- + I_2$$

We failed to isolate the corresponding iodine and fluorine derivatives. Similarly, reaction of $Ag^+C(SO_2CF_3)_3{}^-$ with Me_3SiCl resulted in decomposition. Trimethylsilylane did not react with $HC(SO_2CF_3)_3$.

All reactions of $HC(SO_2CF_3)_3$ or its salts with XeF_2, $Xe(OSeF_5)_2$, or $Xe(OTeF_5)_2$ under various conditions, however, failed to give xenon–carbon-bonded species.

Experimental Section

Materials. CF_3SO_2F, obtained by electrofluorination of CH_3SO_3H, was purchased from the University of Duisburg, Duisburg, West Germany. $CH_2(SO_2CF_3)_2$ was obtained according to a literature method.[7]

General Procedures. Conventional glass vacuum lines were used for transfer of volatile materials. A drybox with a water content of about 0.2 ppm was used for handling moisture-sensitive materials. Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrometer. ^{19}F and ^1H NMR spectra were obtained on a JEOL FX 90Q Fourier transform spectrometer operating at 84.25 and 89.55 MHz, respectively. $CFCl_3$ and TMS were used as external references, and chemical shifts follow IUPAC conventions. Mass spectra were obtained by the EI technique with 70-eV electrons. Elemental analyses were performed by Beller Mikroanalytical Laboratorium, Göttingen, West Germany.

Preparation of Tris((trifluoromethyl)sulfonyl)methane, $HC(SO_2CF_3)_3$, from $H_2C(SO_2CF_3)_2$. A three-necked glass vessel with reflux condenser is loaded with 5 g (18 mmol) of $CH_2(SO_2CF_3)_2$, dissolved in 25 mL of dry tetrahydrofuran. Under strictly anhydrous and oxygen-free conditions 12 mL (36 mmol) of a 3 M solution of methylmagnesium chloride in THF is slowly added. When evolution of methane ceases, the solution is transferred to a 200-mL stainless-steel autoclave. The autoclave is cooled to −196 °C, 4.1 g (27 mmol) of CF_3SO_2F is condensed in, and the mixture is heated for 12 h at 60 °C. After the autoclave is cooled to room temperature, all volatile materials are pumped off. The remaining solid is dissolved in 50 mL of water and the solution acidified with HCl. The solution is then extracted three times with diethyl ether, the combined ether extracts are taken to dryness, and the solid residue is subjected to a vacuum sublimation at 70 °C with unreacted $CH_2(SO_2CF_3)_2$ subliming. The residue of the sublimation is acidified with a few grams of concentrated sulfuric acid and then sublimed several times in vacuo at 80 °C. This crude $HC(SO_2CF_3)_3$ is purified by dissolution in water, and precipitation of $SO_4{}^{2-}$ with $BaCl_2$, and extraction with ether. The ether is evaporated, and the solid is sublimed at 50 °C. The yield is 1.8 g (25%) of colorless, very hygroscopic $HC(SO_2CF_3)_3$, mp 69.2 °C.

Table III. Selected Bond Angles in $K^+C(SO_2CF_3)_3{}^-\cdot H_2O$ (deg)[a]

CS_2	121.6, 121.0, 122.2
SO_2	120.4, 120.7, 119.3
SC_2	106.1, 105.4, 105.54
CF_2	107.3–111.6

[a] Estimated standard deviations 0.2–0.5°.

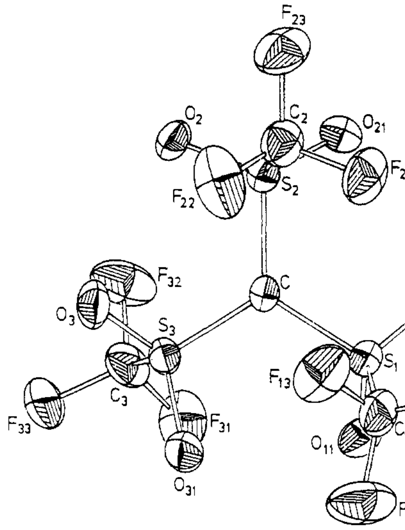

Figure 1. ORTEP drawing of the $C(SO_2CF_3)_3{}^-$ anion, with 50% probability ellipsoids. Note the asymmetry of the CF_3 groups' orientation: two are above the CS_3 plane and one is below. A similar behavior was found for the fluorine atoms in the $C(SO_2F)_3{}^-$ anion.

IR data (in KBr): 2925 m, br, 2477 w, br, 1377 s, 1331 w, 1204 vw, 1123 s, 1075 m, 1026 s, 986 s, 885 m, 852 m, 772 w, 688 m, 629 s, 578 s, 514 s, 456 w, 435 w, 417 m, 394 w, 382 m cm^{-1}. Raman data (solid): 1239 s, 1226 s, 1108 s, 773 vs, 688 s, 660 w, 579 m, 555 m, 533 m, 519 m, 381 s, 372 s, 345 vs, 326 s, 311 vs, 297 s, 284 s, 256 vs, 178 w, 120 s cm^{-1}. ^1H NMR data (CD_3CN): $\Phi = 9.7$. ^{19}F NMR data (CD_3CN): $\Phi = -76.8$. Mass spectral data: *m/e*, 279 ($C_3HF_6S_2O_4{}^+$, 20%), 263 ($C_3HF_6S_2O_3{}^+$, 4%), 133 ($CF_3SO_2{}^+$, 9%), 117 (CF_3SO^+, 10%), 101 (CF_3S^+, 3%), 69 ($CF_3{}^+$, 100%).

Preparation of $Cs^+C(SO_2CF_3)_3{}^-$ and $HC(SO_2CF_3)_3$ Directly from CF_3SO_3F. A 500-mL three-necked flask, equipped with a stirrer and a −78 °C reflux condenser, is charged with 189 mL (0.56 mol) of a 3 M CH_3MgCl solution in THF. With the flask at 0 °C, 69 g (0.45 mol) of CF_3SO_2F is bubbled into the solution over a 3-h period. The temperature is raised to 35–50 °C after two-thirds of the CF_3SO_2F are added. After complete addition, stirring is maintained for 12 h at room temperature. The solvent is pumped off, and 300 mL of 3 M HCl is added to the remaining solid. Several extractions with ether and workup of the combined ether extractions as described above afford 9.5 g of $CH_2(SO_2CF_3)_2$ (24%, based on CF_3SO_2F). The residue of the sublimation, which is a brown, half-solid mass, is dissolved in water, filtered, and neutralized with Cs_2CO_3. The precipitate is recrystallized from water and vacuum dried. A total of 14.85 g of $Cs^+C(SO_2CF_3)_3{}^-$ is obtained, a colorless crystalline solid (20% yield based on CF_3SO_2F). For physical data, see below. $Cs^+C(SO_2CF_3)_3{}^-$ (4 g, 8.8 mmol) is transferred to a sublimator and 10 mL of concentrated H_2SO_4 is added. Sublimation in vacuo at 30 °C onto a −30 °C cold finger and resublimation at 30 °C afford 2.8 g of pure $HC(SO_2CF_3)_3$ (95% yield, based on $CsC(SO_2CF_3)_3)$).

Preparation of $K^+C(SO_2CF_3)_3{}^-\cdot H_2O$, $Rb^+C(SO_2CF_3)_3{}^-$, $Cs^+C(SO_2CF_3)_3{}^-$, and $Ag^+C(SO_2CF_3)_3{}^-$. Stoichiometric amounts of $CH(SO_2CF_3)_3$ and the corresponding metal carbonates are reacted in water. The solubility of the $C(SO_3CF_3)_3{}^-$ salts in water decreases in the order $Ag^+ > K^+ > Rb^+ > Cs^+$. The cesium compound is therefore recrystallized from hot water. The potassium compound is obtained by almost complete evaporation of water at room temperature. The rubidium compound is obtained after partial evaporation of water. The silver compound is obtained by pumping to dryness. It must be protected from light. Freshly prepared, it is colorless like the other salts, but it slowly turns brown, especially in the light.

IR data for $Cs^+C(SO_2CF_3)_3^-$ (in KBr): 2923 w, 2853 w, 1385 s, 1373 vs, 1334 m, 1230 s, 1196 vs, 1131 s, 1121 s, 970 s, 776 w, 765 w, 693 s, 609 s, 584 s, 515 s, 427 w, 393 w, 279 w cm^{-1}. Raman data for $K^+C(SO_2CF_3)_3^-\cdot H_2O$ (solid): 1395 m, 1378 m, 1348 w, 1243 m, 1227 m, 1196 w, 1119, w, sh, 1112 m, 1002 w, 983 w, 773 s, 763 w, sh, 688 m, 577 m, 570 m, sh, 558 m, 535 m, 418 w, 396 m, 384 m, 374 m, 349 s, 329 w, 313 s, 291 s, 275 m, 260 vs, 209 w, 195 m, 187 m, 124 s cm^{-1}.

Anal. Calcd for $C_4F_9O_3S_3Rb$: C, 9.67; F, 34.44; S, 19.34; Rb, 17.22. Found: C, 8.93; F, 34.10; S, 17.78; Rb, 18.47.

Crystallographic Study. A needle-shaped, colorless crystal of $K^+C(SO_2CF_3)_3^-\cdot H_2O$ of approximately 0.3 mm size was obtained by very slow but complete evaporation of the water from an aqueous solution over a period of several days. Intensities were measured on a STOE diffractometer with graphite monochromator, Mo Kα radiation, and Ω scan at room temperature. The space group was determined as $Pc2_1b$ with a = 605.91 (6) pm, b = 1398.77 (8) pm, and c = 1605.60 (13) pm, with a cell volume of 1.36097×10^9 pm^3, $Z = 4$, and calculated density of 2.289 g cm^{-3}. A total of 1255 reflections were measured, 1232 reflections with $I > 2\sigma(I)$; when $+h,+k,+l$, $5° < 2\theta < 50°$. All atoms were anisotropically refined, no extinction corrections were made, and a numerical absorption correction $\mu = 9.6$ cm^{-1} was used. Weighting scheme $W = xy$, $x = 1$ for $\sin \delta > 0.4$, $x = (\sin \delta)/0.4$ for $\sin \delta \leq 0.4$, $y = 1$ for $F_o < 40$, $y = 40/F_o$ for $F_o \geq 40$.

The structure was determined by using a procedure based on intermolecular Patterson vectors, called IMPASS.[8] The method was chosen because the direct methods MULTAN and SHELX failed. Scattering factors from ref 9 were used. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, giving the agreement factors $R = 0.029$, $R_w = 0.028$.

$CCl(SO_2CF_3)_3$. A glass ampule with valve is charged with 0.49 g (0.9 mmol) of $Ag^+C(SO_2CF_3)_3^-$, onto which is condensed 2 mL of dry CH_2Cl_2 and 0.1 g (1.4 mmol) of Cl_2. The suspension is stirred for 2 h at 0 °C. After filtration and evaporation of the solvent from the filtrate, the resulting residue is sublimed from room temperature onto a −30 °C cold finger at 10^{-2} mbar. Colorless $ClC(SO_2CF_3)_3$ is obtained: 0.38 g (90% yield); mp 69.1 °C.

IR data: 2923 w, 2853 w, 2423 w, 1964 w, 1377 vs, 1322 m, 1204 vs, 1124 vs, 983 s, 765 w, 689 m, 630 s, 586 m, 416 w, 386 w cm^{-1}. Raman data: 1418 w, 1407 w, 1220 m, 1194 m, 1095 m, 873 w, 788 w, 770 s, 737 w, 650 w, 582 w, 561 w, 547 w, 525 w, 498 w, 387 s, 367 w, 337 s, 320 m, 301 m, 274 s, 233 s, 200 s, 177 s, 157 vs, 121 w cm^{-1}. ^{19}F NMR data ($CDCl_3$): $\Phi = -60.7$. Mass spectral data: m/e, 297 ($C_3F_6O_3S_2Cl^+$, 2%), 249 ($C_3F_6S_2Cl$, 3%), 145 ($C_2F_3O_2S^+$, 4%), 133 ($CF_3O_2S^+$, 2%), 117 (CF_3OS^+, 10%), 69 (CF_3, 100%).

$CBr(SO_2CF_3)_3$. Bromine (0.2 g, 1.25 mmol) is dissolved in 8 mL of dry CH_2Cl_2 and is slowly added to a suspension of 0.6 g (1.16 mmol) of $Ag^+(SO_2CF_3)_3^-$ in 8 mL of CH_2Cl_2 at 0 °C. Stirring is maintained for 3 h. The precipitate is filtered off and washed with CH_2Cl_2. The combined filtrates are pumped to dryness. The residue is sublimed from room temperature onto a −30 °C cold finger at 10^{-2} mbar. A total yield of 0.44 g (94% yield) of colorless $BrC(SO_2CF_3)_3$ is obtained; mp 93.8 °C.

IR data: 2923 w, 2853 w, 2414 vw, 1972 w, 1378 vs, 1332 m, 1204 vs, 1126 vs, 982 s, 765 w, 689 m, 630 s, 586 s, 516 m, 416 w, 386 w cm^{-1}. Raman data: 1403 m, 1217 m, 1193 w, 1095 m, 808 w, 785 w, 770 m, 730 w, 649 vw, 582 vw, 560 vw, 548 w, 522 vw, 369 s, 320 sh, 311 s, 277 s, 234 vs, 202 vs, 157 vs, 123 cm^{-1}. ^{19}F NMR ($CDCl_3$): $\Phi = -60.3$. Mass spectral data: m/e, 341 ($C_3F_6O_3S_2Br^+$, 2%), 292 ($C_3F_3S_2Br^+$, 1%), 196 (CF_3OSBr^+, 1%), 145 ($C_2F_3O_2S^+$, 12%), 133 ($CF_3O_2S^+$, 6%), 123 ($CSBr^+$, 9%), 107 ($COBr^+$, 16%), 91 (CBr^+, 7%), 69 (CF_3^+, 100%).

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. P. Sartori (Universität Duisburg) for samples of CF_3SO_2F and Prof. J. Fuchs (FU Berlin) for help with the crystal structure determination.

Registry No. $HC(SO_2CF_3)_3$, 60805-12-1; $CH_2(SO_2CF_3)_2$, 428-76-2; CF_3SO_2F, 335-05-7; $Cs^+C(SO_2CF_3)_3^-$, 114395-68-5; $K^+C(SO_2CF_3)_3^-$, 114395-69-6; $Rb^+C(SO_2CF_3)_3^-$, 114395-70-9; $Ag^+C(SO_2CF_3)_3^-$, 114395-71-0; $CCl(SO_2CF_3)_3$, 114395-72-1; $CBr(SO_2CF_3)_3$, 114395-73-2.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond lengths, and bond angles and a packing diagram (6 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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A New Class of (*N*,*N*′-Bis(salicylideneamino)ethanato)iron(II) Complexes: Five-Coordinate $[Fe^{II}(salen)L]^-$. Preparation, Properties, and Mechanism of Electron-Transfer Reactions

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The heterogeneous reaction of the Fe(II) complex Fe(salen) with ligands $L^- = F^-$, Cl^-, OH^-, NCS^-, CN^-, SH^-, and SR^- in acetonitrile afforded the purplish complexes $[Fe(salen)L]^-$, isolated as sodium or Et_4N^+ salts. Also generated in situ was $[Fe(salen)(OC_6H_4\text{-}p\text{-}Me)]^-$. The complexes contain high-spin Fe(II) in a square-pyramidal coordination unit with an axial L^- ligand, exhibit isotropically shifted ^1H NMR spectra of good resolution, and are electrochemically oxidizable to Fe(salen)L in chemically reversible processes. Absorption and NMR spectra clearly indicate the similarity in structure of the complexes, and the isotropic shifts show that the $S = 2$ ground state, established for one complex in the solid and solution states, applies to all. $(Et_4N)[Fe(5\text{-}NO_2salen)(SC_6H_4\text{-}p\text{-}Me)]$ crystallizes in triclinic space group $P\bar{1}$ with a = 9.644 (2) Å, b = 12.115 (3) Å, c = 14.788 (3) Å, α = 98.33 (2)°, β = 105.84 (2)°, γ = 98.41 (2)°, and $Z = 2$. With use of 3483 unique data ($F_o^2 > 3\sigma(F_o^2)$), the structure was refined to R (R_w) = 4.5% (6.1%). The anion contains Fe(II) in a somewhat distorted-square-pyramidal geometry with the sulfur atom in the axial position. The Fe atom is displaced 0.49 Å above the O_2N_2 mean plane, with a Fe–S bond distance of 2.386 (2) Å. The structure is similar to those of $[Fe(P)SR]^-$ complexes (P = porphyrinate) and is assumed to apply to all members of the set. Selected reactions Fe(salen)L + $[Fe(salen)L']^-$ in acetone result in electron transfer or ligand exchange and have been examined by ^1H NMR spectroscopy. A mechanism involving a doubly bridged binuclear intermediate is proposed and provides fresh insight into how coordinatively unsaturated complexes of this type may undergo electron transfer and ligand exchange.

Introduction

The chemistry of $Fe^{III}(salen)L$ complexes (salen = *N*,*N*′-bis(salicylideneamino)ethanato(2−)) has been extensively investigated since the original synthesis of several examples of this class by Pfeiffer et al., whose major contribution in 1933 in effect opened the field of Schiff base complexes.[2] A large variety of anionic ligands L, including halide, pseudohalide, carboxylate, phenolate, and thiolate, have been shown to form stable, mononuclear, high-spin complexes[2-13] that have a distorted-square-pyramidal

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