calculation on HCN first and adopted the obtained H_{ii}'s (C 2s, 180.9×10^3 cm^{-1}; C 2p, 92.7×10^3 cm^{-1}; N 2s, 206.9×10^3 cm^{-1}; N 2p, 93.7×10^3 cm^{-1}) for the calculations on the actual complexes, only iterating the H_{ii}'s of Mo and S. The influence of S 3d orbitals was tested by using the optimized orbital exponent 1.7077[54] and the VOIP parameters of McGlynn et al.[55]

Registry No. **1a**, 97278-52-9; **2a**, 72609-97-3; **2b**, 97278-54-1; **2c**, 97278-53-0; **3a**, 71934-12-8; **4a**, 97278-56-3; **4b**, 97278-61-0; **5a**, 25531-12-8; **6a**, 97278-57-4; $[(C_6H_5)_4P]_2MoS_4$, 14348-10-8; $[(C_6H_5)_4P]_2MoOS_3$, 83061-15-8; $Mo_2S_4(dtc)_2$, 36539-27-2; $[(C_6H_5)_4P]_2[Mo_2(S_2)_6]$, 97278-59-6; $NH_4K[Mo_4(NO)_4(S_2)_6O]$, 97278-60-9; $K_8[Mo_4S_4(NO)_4(CN)_8]$, 97335-14-3; S, 7704-34-9; Mo, 7439-98-7.

Supplementary Material Available: Thermal parameters (Tables SI and SIII) and structure factor amplitudes (Tables SII and SIV) for **2b** and **4b** (23 pages). Ordering information is given on any current masthead page.

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Solid-State and Solution Properties of (*N*,*N*'-Ethylenebis(salicylideneaminato))(nitrato)iron(III) and Related Complexes

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Two solid-state forms of the title complex, Fe(salen)NO_3, were prepared by reacting a methylene chloride solution of $[Fe(salen)]_2O$ with aqueous 0.5 M nitric acid and precipitating the complex either with ether or with pentane. The form isolated from pentane was dimeric with a unidentate nitrate bound to each iron, $[Fe(salen)ONO_2]_2$, while the other form was monomeric with a bidentate nitrate, Fe(salen)O_2NO. The reaction was carried out with three other salicylideneamine iron(III) μ-oxo complexes, and only the dimeric, unidentate nitrate form of each was prepared. The ^{15}N-labeled nitrate complexes were used to assign the nitrate infrared bands. The ^{57}Fe Mössbauer spectra and magnetic susceptibilities of the complexes were compared to similar data for the tetraphenylporphyrin complex Fe(TPP)O_2NO, which is monomeric with a bidentate nitrate. The proton NMR spectra of the two forms of Fe(salen)NO_3 in solution were identical, as were the solution infrared spectra, and such spectra indicated that the solution species were monomeric with bidentate nitrate ligands.

Introduction

Iron nitrate complexes have only been studied to a limited extent,[1-5] even though a wide variety of other metal nitrate complexes have been reported and used to describe the binding of nitrate to metal ions.[6-10] Of the iron nitrates known, most are iron(III) since iron(II) is expected to reduce nitrate.[11] However, $(C_5H_5)Fe(CO)_2(NO_3)$, with iron in a reduced oxidation state, has been reported[12] and its structure shows a unidentate-bound nitrate.[5] Recent experiments have pointed out a need for more information on iron(III) nitrates.

A methylene chloride solution of $[Fe(salen)]_2O$[13] has been shown recently[14] to react rapidly with nitric oxide and dioxygen to produce, upon solvent removal, a fine black powder with the apparent formula Fe(salen)NO_3. The black powder has proven to be an interesting material since it can serve as a powerful nitrosating agent.[14] When heated with a methylene chloride or toluene solution containing a secondary amine, such as pyrrolidine or morpholine, the powder produced a high yield of the carcinogenic *N*-nitrosamine. Because of the possible involvement of the biologically important species iron and nitrate in *N*-nitrosamine production, the black powder and the nitrosation reactions are under study at this time. In order to proceed with this study, it was necessary to have some detailed information on iron(III) salicylideneamine nitrate complexes.

Since there was some uncertainty about the nature of the black powder, a more direct preparative procedure for the iron(III) salicylideneamine nitrates was needed. The iron(III) nitrate, Fe(TPP)O_2NO, described by Goff and co-workers,[1] were prepared by reacting a methylene chloride solution of $[Fe(TPP)]_2O$ with an aqueous 6 M nitric acid solution and isolating the product from the organic layer. When we reacted a methylene chloride solution of $[Fe(salen)]_2O$ with dilute nitric acid and varied the conditions of product isolation, two different nitrate complexes were obtained. One appeared to be dimeric, similar to $[Fe(salen)Cl]_2$,[15] while the other was like Fe(TPP)O_2NO—monomeric with a bidentate nitrate.[1] Below, these and other salicylideneamine iron(III) nitrate complexes are discussed and compared with Fe(TPP)O_2NO.

Experimental Section

Chemicals. All reagents and solvents were reagent grade. Methylene chloride and toluene were purified by standard procedures.[16] Salicylaldehyde was vacuum distilled, and ethylenediamine and propylenediamine were vaccum distilled from KOH. The salicylideneamine ligands (H_2L) were prepared by reacting two parts of the salicylaldehyde with

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(13) Abbreviations: salicylideneamine ligands (H_2L) H_2salen, *N*,*N*'-ethylenebis(salicylideneamine); H_2salpn, *N*,*N*'-propylenebis(salicylideneamine); H_2(5-Clsalen), *N*,*N*'-ethylenebis(5-chlorosalicylideneamine); H_2(5-MeOsalen), *N*,*N*'-ethylenebis(5-methoxysalicylideneamine); porphyrin ligand H_2TPP, *meso*-tetraphenylporphyrin.

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one part of the diamine in methanol with use of literature procedures.[17-19] They were recrystallized from alcohol. The μ-oxo complexes, (FeL)$_2$O, were prepared by the procedure of Mitchell et al.[20] and were recrystallized from methanol, except for the 5-Clsalen complex, which was recrystallized from pyridine. [Fe(TPP)]$_2$O was obtained from Mid-Century Chemicals Inc. (Posen, IL). Analyses were performed by Galbraith Labs (Knoxville, TN).

Iron Nitrate Complexes. The procedure of Phillipi et al.[1] was followed to prepare Fe(TPP)O$_2$NO. We found that shaking 6 M nitric acid with a methylene chloride solution of the μ-oxo complex for 15 min, as suggested by the authors, resulted in some significant changes in the visible spectrum of the complexes. This might be due to porphyrin ring nitration or oxidation[21] since analysis showed a larger nitrogen to iron ratio than expected. A shaking time of no more than 5 min was adequate for nitrate complex formation. With the more acid-sensitive salicylideneamine complexes, a shorter shaking time and more dilute acid was used.

The Fe(salen)NO$_3$ complexes were prepared by dissolving [Fe(salen)]$_2$O (1.5 g, 2.3 mmol) in methylene chloride (200 mL), adding 14 mL of freshly boiled 0.5 M HNO$_3$, and shaking the mixture for 3 min. The aqueous phase was removed. If ether (200 mL) was added and the mixture allowed to stand for 12 h, crystals that appeared to be the monomeric form, Fe(salen)O$_2$NO, were isolated. If pentane (200 mL) was added instead of ether, then crystals of the dimeric form, [Fe(salen)ONO$_2$]$_2$, resulted. If the monomer was dissolved in methylene chloride and an equal volume of pentane added, the dimer slowly precipitated out of solution. Dissolving the dimer in methylene chloride and then adding ether produced monomer precipitation, in most instances.

To prepare the other salicylideneamine iron(III) nitrates, the following general procedure was used: the μ-oxo complex, (FeL)$_2$O (1.5 g), was dissolved in methylene chloride (100 mL), the solution cooled to 0 °C, and cold, freshly boiled 1 M HNO$_3$ (6 mL) added. The mixture was shaken for about 1 min and the aqueous layer rapidly removed. If cold ether (200 mL) was added slowly and the solution allowed to stand for 4 days at 0 °C, crystals of the dimer resulted. Attempts to prepare the monomeric forms led only to monomer–dimer mixtures.

All solid products were dried under vacuum at 70 °C for 24 h.

The above procedures were used on a smaller scale (ca. one-fifth) to prepare the ^{15}N-labeled nitrate complexes, Fe(L)^{15}NO$_3$. Nitric acid (99 atom % ^{15}N, Stohler Isotope Chemical) was used.

[Fe(salen)ONO$_2$]$_2$: Mass spectrum (50 eV, *m/e* (relative intensity)) 384 (28), 338 (13), 322 (100); IR (cm^{-1} mull) nitrate bands 1486, 1283, 1033, 815 (obsd at 77 K), dimer bands 889, 863; electronic spectrum[22] (λ_{max}, nm (log ϵ_{max})) 525 (3.67), 321 (4.05); magnetic data[23] (room temperature) χ_m 0.0113, 5.2 μ_B, diamagnetic correction −380 × 10^{-6}. Anal. Calcd for $C_{16}H_{14}N_3O_5Fe$: N, 10.94; Fe, 14.54. Found: N, 10.82; Fe, 14.52; N/Fe ratio, 2.97.

[Fe(salen)O^{15}NO$_2$]$_2$: IR (cm^{-1}, mull) nitrate bands 1454, 1262, 1013, 801.

Fe(salen)O$_2$NO: Mass spectrum (50 eV, *m/e* (relative intensity)) 384 (17), 338 (5), 322 (100); IR (cm^{-1}, mull) nitrate bands 1533, 1252, 1015, 777; electronic spectrum (λ_{max}, nm (log ϵ_{max}) 525 (3.57), 322 (3.98); magnetic data (room temperature) χ_m 0.0131, 5.8 μ_B, diamagnetic correction −180 × 10^{-6}. Anal. Calcd for $C_{16}H_{14}N_3O_5Fe$: N, 10.94; Fe, 14.54. Found: N, 10.70; Fe, 14.21; N/Fe ratio, 3.00.

Fe(salen)O$_2$^{15}NO: IR (cm^{-1}, mull) nitrate bands 1499, 1227, 995, 769.

[Fe(salpn)ONO$_2$]$_2$: Mass spectrum (50 eV, *m/e* (relative intensity)) 398 (16), 352 (5), 336 (100); IR (cm^{-1}, mull) nitrate bands 1482, 1275, 990, ca. 800, dimer bands 890, 860; electronic spectrum λ_{max}, nm (log ϵ_{max}) 525 nm (3.63); magnetic data (room temperature) χ_m 0.0110, 5.1 μ_B, diamagnetic correction −200 × 10^{-6}. Anal. Calcd for $C_{17}H_{16}N_3O_5Fe$: N, 10.56; Fe, 14.03. Found: N, 10.44; Fe, 14.27; N/Fe ratio, 2.92.

[Fe(salpn)O^{15}NO$_2$]$_2$: IR (cm^{-1}, mull) nitrate bands 1440, 1250, 980, 790.

[Fe(5-Clsalen)ONO$_2$]$_2$: Mass spectrum (50 eV, *m/e* (relative intensity)) 453 (11), 407 (7), 391 (100); IR (cm^{-1} mull) nitrate bands 1477, 1280, 1000, 810, dimer bands 885, 870, 860; electronic spectrum (λ_{max}, nm (log ϵ_{max})) 531 nm (3.57); magnetic data (room temperature) χ_m 0.0116, 5.2 μ_B, diamagnetic correction −210× 10^{-6}. Anal. Calcd for $C_{16}H_{12}N_3Cl_2O_5Fe$: N, 9.28; Fe, 12.33. Found: N, 8.95; Fe, 12.04; N/Fe ratio, 2.96.

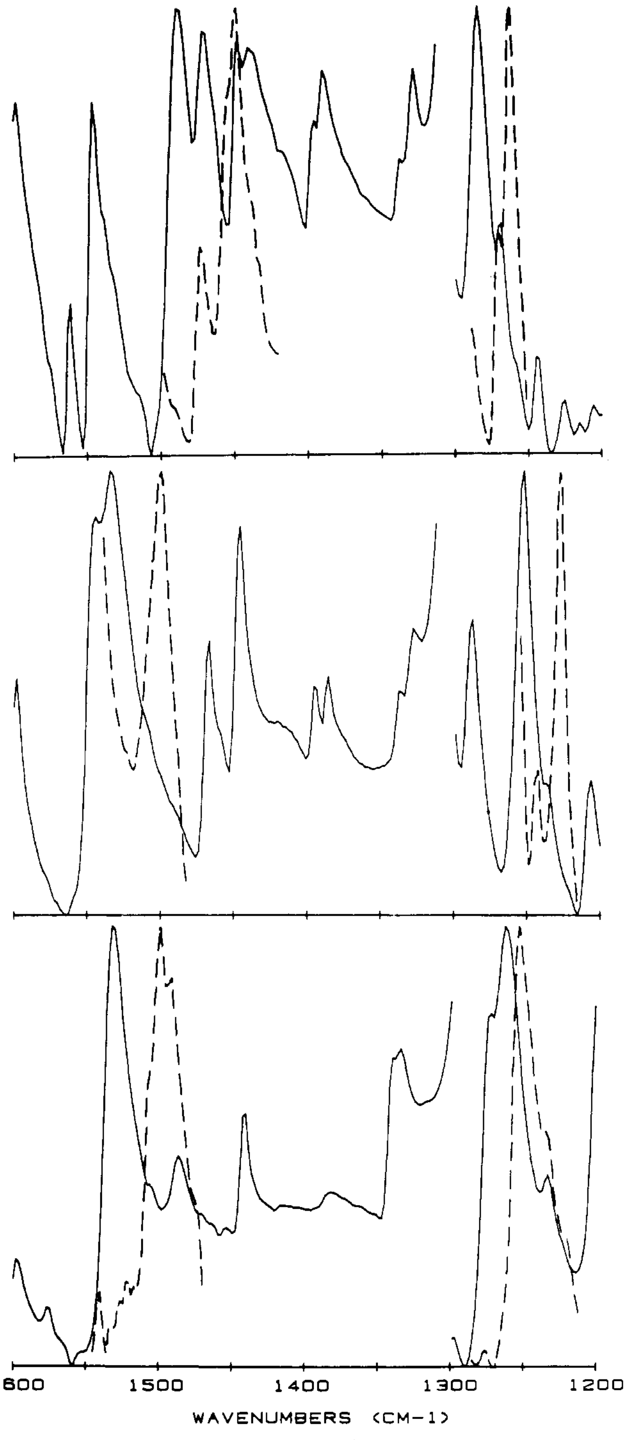

Figure 1. Fluorocarbon (1600–1300 cm^{-1}) and mineral oil (1300–1200 cm^{-1}) absorbance infrared spectra of (top) [Fe(salen)ONO$_2$], (middle) Fe(salen)O$_2$NO, and (bottom) Fe(TPP)O$_2$NO. Dashed lines show important spectral bands of the [^{15}N]nitrate labeled compounds.

[Fe(5-Clsalen)O^{15}NO$_2$]$_2$: IR (cm^{-1} mull) nitrate bands 1448, 1260, 994, 790.

[Fe(5-MeOsalen)ONO$_2$]$_2$: Mass spectrum (50 eV, *m/e* (relative intensity)) 444 (17), 398 (8), 382 (100), IR (cm^{-1}, mull) nitrate bands 1475, 1282, 1010, dimer bands 890, 860, 845 cm^{-1}; electronic spectrum (λ_{max}, nm (log ϵ_{max})) 587 (3.63), 479 sh (3.4), 368 sh (3.8); magnetic data (room temperature) χ_m 0.0110, 5.1 μ_B, diamagnetic correction −350 × 10^{-6}. Anal. Calcd for $C_{18}H_{18}N_3O_7Fe$: N, 9.46; Fe, 12.57. Found: N, 9.01; Fe, 12.11; N/Fe ratio, 2.97.

[Fe(5-MeOsalen)O^{15}NO$_2$]$_2$: IR (cm^{-1}, mull) nitrate bands 1430, 1260, 1005.

Fe(TPP)O$_2$NO: IR (cm^{-1}, mull) nitrate bands 1533, 1262; electronic spectrum (λ_{max}, nm (log ϵ_{max}) 688 (3.30), 658 (3.30), 574 (3.60), 513 (4.02), 412 (5.00); magnetic data (room temperature) χ_m 0.0130, 5.6 μ_B,

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diamagnetic correction -500×10^{-6}. Anal. Calcd for $C_{44}H_{28}N_5O_3Fe$: N, 9.59; Fe, 7.64. Calcd for $C_{45}H_{30}N_5Cl_2O_3Fe$ ($Fe(TPP)NO_3 \cdot CH_2Cl_2$): N, 8.59; Fe, 6.85. Found: N, 8.83; Fe, 6.99; N/Fe ratio, 5.04.

$Fe(TPP)O_2{}^{15}NO$: IR (cm^{-1}, mull) nitrate bands 1497, 1252.

Instrumentation. Infrared spectra were recorded on a Nicolet Model 5DX spectrometer or on a Perkin-Elmer Model 621 spectrometer. The absorbance spectra shown in Figure 1 were obtained on the Nicolet instrument. The spectra in Figure 1 were made with 100 scans with no smoothing being done. Water and carbon dioxide bands were removed from the spectra by purging of the instrument with nitrogen or by spectral subtraction. All of the infrared spectra were taken for samples in mineral oil or fluorocarbon mulls on a KRS-5 plate or in solution with use of KRS-5 solution cells. Spectra at liquid-nitrogen temperature were obtained with a Research and Industrial Instruments Co. Model VLT-2 variable-temperature cell.

For Raman spectra, 5–20 mg of powdered sample was mixed with 250 mg of KCl and pressed at 6000 psi into a rotating sample holder.[24] Samples were irradiated with the green line (5145 Å) of a Spectra-Physics argon ion laser (Model 165). A prism monochromator[24] was used to disperse the laser plasma lines off of the laser axis. The scattered light was collected and focused onto the entrance slit of a SPEX 1403 double monochromator. Spectral slit widths of 2.0 cm^{-1} were used. The pertinent details of the Raman spectrometer have been described.[25] From 8 to 12 scans were collected for each spectrum. The pressed KCl/sample mixtures were checked for decomposition with use of infrared spectroscopy, and none was found.

Mass spectra were obtained by Frank Pittman on a Hewlett-Packard 5985A GC/MS system. Visible spectra were obtained with a Bausch and Lomb Spectronic 2000 spectrophotometer. Thermal gravimetric analyses were carried out with Du Pont Instruments Model 950 thermogravimetric analyzer and Model 990 thermal analyzer, at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Mössbauer spectra were measured with an Austin Science Associates, Inc., constant-acceleration spectrometer using a 1024-channel Canberra Model 30 multichannel analyzer. The ^{57}Co (Rh matrix) source (New England Nuclear) had an intensity of ca. 30 mCi. An Austin Science cryogenic Dewar was used to obtain spectra at liquid-nitrogen temperature. All spectral samples contained from 5 to 15 mg of natural iron/cm^2, sandwiched between Mylar windows. The spectral parameters were calculated with a modified version of the National Bureau of Standards program.[26] Isomer shifts are reported relative to iron foil.

Magnetic susceptibility measurements at room temperature were made on a Faraday balance under a He atmosphere with a Cahn RG electrobalance and an Alfa Scientific AL7500M electromagnet. $HgCo(NCS)_4$ served as calibrant, and measurements were made at three different magnetic field strengths. An average of the three magnetic susceptibilities is reported. The variable-temperature magnetic susceptibility measurement on $[Fe(salen)ONO_2]_2$ was made by Dr. D. L. Karraker of the Savannah River Laboratory, Aiken, SC, using a PAL vibrating-sample magnetometer. The measurement on $Fe(salen)O_2NO$ was made by Dr. R. L. Fagaly of the S.H.E. Corp., San Diego, CA, using S.H.E. Model VTS-905 variable-temperature susceptometer. The program used to analyze the temperature magnetic susceptibility measurements on $[Fe(salen)ONO_2]_2$ was supplied by Dr. A. Vitale of the Liberia Universita Degli Studi di Trento, Trento, Italy.

The proton NMR spectra were recorded on JEOL FX-90Q FT-NMR spectrometer operating at 89.99 MHz. The solutions examined by NMR were made 10 mM in the given Fe compound with use of $CDCl_3$, CD_2Cl_2, and acetone-d_6 (Wilmad Glass Co.) as solvents.

Results and Discussion

Preparation and Analyses. The dimeric, unidentate nitrato complex $[Fe(L)ONO_2]_2$ formed with each of the salicylideneamines. Only with the salen ligand was it possible to obtain the monomeric, bidentate nitrato complex, $Fe(salen)O_2NO$. Trying several recrystallization solvents and temperatures might eventually lead to the isolation of the solid monomeric form with all of the salicylideneamine complexes. However, the easy conversion of the solid monomeric salen complex to the dimer, through solution workup, seems to emphasize the high stability of the dimeric form in the solid state. These results are similar to those found for other iron(III) salicylideneamine complexes, where the ability to form monomeric complexes in the solid depends on the substituents on the salicylideneamine ring and the nature of the axial ligand.[27]

Each sample of $Fe(TPP)O_2NO$ used had precisely the electronic spectra reported in ref 1. For the one sample analyzed, the % N and % Fe values were somewhat low; however, the N to Fe ratio was the expected value. Presumably the low values were due to solvent retention. No evidence of $[Fe(TPP)]_2O$ was shown in the infrared[28] and NMR[29] spectra of the samples.

Mass spectra of the (nitrato)iron(III) salicylideneamine complexes had peaks due to the species M^+, $M^+ - NO_2$, and $M^+ - NO_3$, with the $M^+ - NO_3$ being the most intense. No peak due to the dimer ($M^+{}_2$) was observed.

The solid-state differences between $Fe(salen)O_2NO$ and $[Fe(salen)ONO_2]_2$ were shown by thermal analyses in nitrogen from 30 to 365 °C. The TGA curve of the dimeric complex showed a gradual weight loss beginning at 190 °C and continuing until 220 °C with a total percent weight loss of 9.0%. The monomer showed two distinct zones of weight loss—one at 207 °C with a 2.9% weight loss and the second at 238 °C with a loss of 6.1%.

Infrared and Raman Spectra. Infrared spectroscopy was the primary method used to distinguish the nitrate binding in each of the solid-state forms. Nitrate bands were identified by comparing the mull spectra (mineral oil and fluorocarbon) of the compounds with each other and with the spectrum of the corresponding [^{15}N]nitrate labeled compound. The room-temperature absorbance spectra for unlabeled and labeled $[Fe(salen)ONO_2]_2$, $Fe(salen)O_2NO$, and $Fe(TPP)O_2NO$ in 1600–1200 cm^{-1} region are shown in Figure 1. For the dimeric complexes, bands due to the nitrate ion were observed around 1480, 1280, 1030, and 800 cm^{-1}. In the ^{15}N-labeled compounds the band at 1480 cm^{-1} was shifted to a lower wavenumber by about 30 cm^{-1}, while the bands at 1280, 1030, and 800 cm^{-1} were shifted by about 20 cm^{-1}. If there was uncertainty in a band assignment, the spectrum at liquid-nitrogen temperature, with its improved resolution, was obtained. The assignments of the two highest wavenumber bands were easily made, but the two lower wavenumber bands were more difficult to assign and some error may exist in these values.

The bidentate salen (nitrato)iron(III) complex had the two highest frequency nitrate bands (1534 and 1252 cm^{-1}) at about the same wavenumbers as $Fe(TPP)O_2NO$ (1533 and 1262 cm^{-1}). The salen complex showed two other nitrate bands at 1015 and 777 cm^{-1}, while similar bands for the TPP complex were overlapped by intense TPP bands. The ligand bands were identified from spectra of the (μ-oxo)- and chloroiron(III) complexes. As with the unidentate complexes, the ^{15}N-labeled bidentate complexes had nitrate bands at lower wavenumbers than those for the unlabeled compounds.

The presence of four bands in the 1600–800-cm^{-1} region due to bound nitrate is expected, the typical ranges being as follows:[7] bidentate, 1500 ± 15, 1235 ± 25, 1010 ± 10, 810 ± 10 cm^{-1}; unidentate, 1450 ± 40, 1300 ± 25, 1000, 810 ± 15 cm^{-1}. The bands for the salicylidenamine and porphyrin iron(III) nitrate complexes are within, or close to, the ranges shown above. It has been pointed out that the separation between the two highest wavenumber bands is a useful criterion for distinguishing between the unidentate and bidentate nitrato complexes, with the unidentate form expected to have a smaller band separation than the bidentate complexes.[7]

Infrared spectroscopy has been recognized to be a difficult tool to use to distinguish between unidentate- and bidentate-coordinated nitrate, especially if a complex ligand like salen is present.[30] However, this was the only technique available to us for nitrate bonding mode identification. Through the use of ^{15}N isotope labeling, low-temperature infrared spectra, and the spectra of a solid of known structure, we feel the assignments of the bonding modes are correct.

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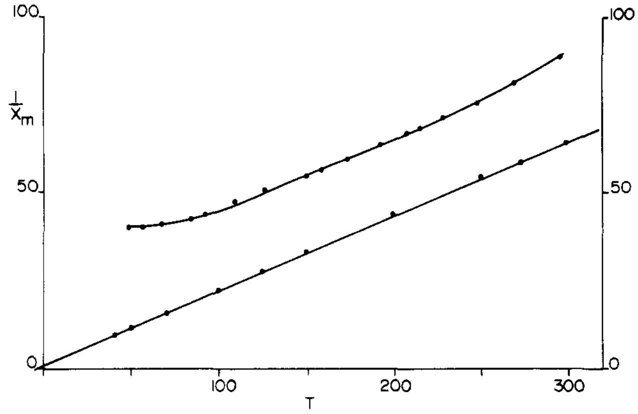

Figure 2. Reciprocal of the molar magnetic susceptibility vs. the absolute temperature for (top) [Fe(salen)ONO$_2$]$_2$ and (bottom) Fe(salen)O$_2$NO. The curve for [Fe(salen)ONO$_2$]$_2$ was calculated by the equation in ref 36.

A reviewer suggested that the Raman spectra of the nitrate complexes should, according to ref 7, provide further evidence of the coordinating nature of the nitrate. The Raman spectra of the nitrate nitrogen labeled and unlabeled complexes in a pressed KCl matrix were measured. Figure S1 of the supplementary material presents the spectra of the two salen unlabeled complexes. Differences were found around 1300 cm^{-1} (dimer 1313, 1336 cm^{-1}; monomer 1287, 1310, 1331 cm^{-1}) and around 1600 cm^{-1} (dimer 1603, 1620, 1633, 1637 cm^{-1}; monomer 1602, 1639). Otherwise, the spectra were essentially identical. The labeled complexes had the same spectra as the equivalent unlabeled ones. A comparison of these spectra showed no nitrate bands. Apparently, these bands are just too weak relative to the ligand bands to be observed. The spectral differences are no doubt a result of the differences in complex symmetries.

Infrared bands due to the dimer formation of Fe(L)X (L = salicylideneamine), where X = Cl, N$_3$, or NCS, have been observed in the 800–900-cm^{-1} region.[27] These bands are especially prominent at about 890, 860, and 850 cm^{-1}. [Fe(salen)ONO$_2$]$_2$ showed the presence of at least two of these bands. The other dimeric salicylideneamine complexes also showed some of the bands, but in several cases strong ligand bands overlapped them.

Magnetic Susceptibility Measurements. Room-temperature measurements were made on the compounds, and all of the dimeric complexes had magnetic moments of 5.1–5.2 μ_B, while the monomeric complexes had moments of 5.5–5.8 μ_B. Variable-temperature data were obtained for the two salen complexes (Figure 2).[31] The monomeric complex with an approximately normal moment of 5.8 μ_B obeyed the Curie–Weiss law from 300 to 40 K.[32] The data for [Fe(salen)ONO$_2$]$_2$, obtained from 296 to 47 K, showed a lower moment and magnetic exchange interaction similar to that observed with other dimeric iron(III) salen complexes having monodentate anions.[19,27,33-35] Those complexes with dimer bands in their infrared spectra had low moments.

With use of an equation for the molar paramagnetic susceptibility for two $S = {}^5/_2$ ions in an exchange-coupled dimer,[36] a value for J, the exchange parameter, estimated by a least-squares fitting method, was found to be -6 ± 1 cm^{-1}. This is in the range expected for the dimeric association that occurs by the bridging of basal plane salicylideneamine oxygens between the two irons.[19,37]

Table I. Isomer Shift (δ) and Quadrupole Splitting (Δ) Data at Liquid-Nitrogen Temperature for Iron(III) Macrocyclic Nitrates and Related Compounds

			ratios^c		
compd^a	δ,^{b} mm s^{-1}	Δ, mm s^{-1}	intens	width	area
Fe(salen)O$_2$NO	0.49	1.55	0.92	1.15	1.05
[Fe(salen)ONO$_2$]$_2$	0.51	1.55	1.15	0.83	0.9k
[Fe(salpn)ONO$_2$]$_2$	0.49	1.75	0.90	1.15	1.03
[Fe(5-Clsalen)ONO$_2$]$_2$	0.51	1.38	1.15	0.83	0.96
[Fe(5-MeOsalen)-ONO$_2$]$_2$	0.56	1.40	1.15	0.79	0.91
Fe(TPP)O$_2$NO	0.51	0.98	0.50	1.91	1.02
[Fe(salen)Cl]$_2$^{d}	0.47	1.43	0.68	1.50	0.98
Fe(salen)Cl·xCH$_3$NO$_2$^{e}	0.42	1.44	0.58	1.70	1.03
Fe(TPP)Cl^f	0.30	0.48	4.2 K		
Fe(TPP)OMe^g	0.29	0.56	4.2 K		
[Fe(salen)tfa]$_2$^{h}	0.41	1.40	90 K		
Fe(salen)pico^h	0.54	0.91	90 K		

^{a}See footnote 13 for abbreviations. ^{b}Fe reference. ^{c}Value for high-velocity peak divided by low-velocity peak value. ^{d}Unpublished data. ^{e}Reference 41. ^{f}Reference 39, broad high-velocity peak at high temperature. ^{g}Reference 39, broad low-velocity peak at high temperature. ^{h}Reference 35; tfa = trifluoroacetate anion; pico = picolinate anion.

Some of the high-spin, monomeric complexes, expected to have magnetic moments of 5.9 μ_B,[19,27,37,38] had slightly lower values. These values may be caused by the inclusion of solvent in the compound or the presence of a small amount of the μ-oxo complex.

^{57}Fe Mössbauer Spectra. The spectrum of each of the nitrato complexes at liquid-nitrogen temperature showed two asymmetric peaks, typical of high-spin, square-pyramidal iron(III) complexes.[39] The spectral data are given in Table I, along with comparative data for related Fe(III) complexes. The isomer shift range for the nitrato complexes is from 0.40 to 0.56 mm s^{-1}. The quadrupole splitting values range from 0.98 to 1.75 mm s^{-1}. The peak asymmetry is described by ratios (high-velocity peak value divided by low-velocity peak value) of intensities, full widths at half-height, and areas of the two peaks. Room-temperature spectra (data not given) had isomer shifts that were about 0.1 mm s^{-1} greater than the liquid-nitrogen-temperature values, as expected considering the second-order Doppler shift behavior. The room-temperature quadrupole splitting values changed by no more than 0.02 mm s^{-1}, and the peaks were only slightly more asymmetric.

The isomer shifts for the nitrate complexes are in the same range as those for other similar complexes, with the exception of the large value for Fe(TPP)O$_2$NO. The crystal structure of Fe(TPP)O$_2$NO shows the iron displaced 0.60 Å out of the mean porphyrin plane toward the unsymmetrical bidentate nitrate.[1] Most high-spin, five-coordinate iron(III) porphyrin complexes with unidentate, anionic ligands have the iron displaced by a smaller amount.[40] The larger displacement for the nitrate complex would be expected to increase tetragonal distortion and lead to the large quadrupole splitting values.

The dimeric and monomeric Fe(salen)NO$_3$ complexes had approximately the same Mössbauer parameters; however, the peak asymmetry was different. The monomer had a broad, less intense high-velocity peak, while the dimer had a broad, less intense low-velocity peak. Since some of the dimeric salicylideneamine complexes had the same peak asymmetry as Fe(salen)O$_2$NO, the nature of the peak asymmetry does not seem to be a distinguishing characteristic of complex molecularity.

It is interesting to note the large variation in peak asymmetry for the nitrate and related complexes. The Mössbauer spectra

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(31) The data for [Fe(salen)ONO$_2$]$_2$ and Fe(salen)O$_2$NO used to produce Figure 2 are in Supplementary Table SI.

(32) We obtained a room-temperature moment of 5.9 μ_B for Fe(salen)O$_2$NO, while the measurements made by the S.H.E. Corp. gave a value of 6.1 μ_B. This discrepancy should not affect the linear nature of the Curie–Weiss plot in Figure 2.

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Table II. Proton NMR Chemical Shifts of Fe(salen)X Complexes[a]

X	solvent	T, °C	salen shifts, δ			
			3-H	4-H	5-H	6-H
Cl^-	$CDCl_3$	30	+83	−78	+69	−49
Cl^-	CD_2Cl_2	30	+82	−78	+68	−49
Cl^-	acetone-d_6	28	+84	−78	+67	−49
NO_3^-	$CDCl_3$	30	+96	−82	+81	−53
NO_3^-	CD_2Cl_2	30	+97	−82	+81	−53
NO_3^-	acetone-d_6	28	+95	−82	+79	−53
Cl^{-b}	$CDCl_3$	27	+84	−80	+70	−50
acetate[b]	$CDCl_3$	27	+83	−78	+69	−48
benzoate[b]	$CDCl_3$	27	+84	−79	+70	−48

[a] All shifts are relative to Me_4Si with downfield shifts negative. [b] Reference 46.

Table III. Proton NMR Chemical Shifts of $Fe(salen)NO_3$ in $CDCl_3$ at Different Temperatures[a]

	salen shifts, δ		
	4-H	5-H	6-H
313 K	−80.0	+78.1	−52.0
303 K	−82.2	+80.6	−53.3
281 K	−88.6	+88.2	−57.4
263 K	−94.4	+94.8	−60.8
243 K	−101.4	+103.5	−66.0
slope ($\times 10^4$)[b]	−2.3	+2.7	−1.5
intercept[b]	−6.3	−9.4	−4.0
cc[c]	0.999	0.999	0.999

[a] The 3-H shift was too broad to measure precisely. [b] Linear regression analysis results. [c] Correlation coefficient.

of salicylideneamine[33-35,41-44] and porphyrin iron(III) chlorides[38,39] show broad, high-velocity peaks, while those of the porphyrin iron(III) methoxides[39] show broad, low-velocity peaks. The asymmetry is due primarily to a paramagnetic relaxation effect with one of the nuclear transitions being affected more than the other, resulting in an unequal amount of peak broadening. Mössbauer spectra taken with samples in an applied magnetic field should provide an explanation for the variation in peak asymmetry found with the nitrate complexes.[44]

The Mössbauer and infrared spectra of $Fe(TPP)O_2NO$ both showed a small amount of $[Fe(TPP)]_2O$ to be present in solid samples of 1 month or more old. The amount seemed to increase with time even though the solid was stored in a desiccator. The other solid nitrate complexes did not show this instability. Phillipi et al.[1] found that $Fe(TPP)O_2NO$ in dry chloroform solution converted to the μ-oxo complex after several hours.

Solution Studies. The proton NMR spectra of the dimer and monomer forms of $Fe(salen)NO_3$ were obtained in deuterated chloroform, methylene chloride, and acetone. The two forms in each solvent gave identical spectra; however, small differences between spectra taken in different solvents were found. The chemical shifts for the phenyl ring protons of salen are given in Table II along with values for other Fe(salen)X compounds. The shifts for the nitrate complex have the expected signs, but the values are larger than those for the chloride, acetate, and benzoate complexes,[45] all of which have about the same shift values. A sample of Fe(salen)Cl was prepared,[15] and the NMR spectra were obtained in the various solvents and at the slightly higher probe temperature to ensure that these factors did not contribute to the observed differences.

A difference in the mode of bonding by the X ligand to the iron may account for the NMR spectral differences between the nitrate complex and the chloride, acetate, and benzoate complexes. In solution Fe(salen)Cl is monomeric with a unidentate ligand,[27] as might be expected for the acetate and benzoate complexes. The nitrate, on the other hand, may be bound in a bidentate manner like that found for $Fe(TPP)O_2NO$ in solution.[1] The coordination mode of the nitrate in dissolved $Fe(TPP)O_2NO$ was ascertained by assuming a correlation existed between the X ligand coordination mode and the NMR shift pattern of the complex. For the porphyrin complex, bidentate nitrate coordination produced a reduction in the pyrrole shift values from those found with unidentate ligands. This would be expected if the paramagnetic metal ion was displaced from the porphyrin ring by the bidentate ligand more than by the unidentate one. The crystal structure of $Fe(TPP)O_2NO$ shows this to be the case. Bidentate coordination of the nitrate in the salen complex would distort the salen ring to a nonplanar cis-β configuration.[46] This should lead to a change in the salen shift values compared to those values obtained with a unidentate axial ligand and a more planar macrocycle. A full discussion of the observed shifts will have to wait until more structural information is available on the monomeric salen complex.

Proton NMR spectra of $Fe(salen)NO_3$ were obtained in deuterated chloroform from −30 to +40 °C (Table III). A plot of the chemical shifts vs. $1/T$ for each of the proton signals was linear. When $[Fe(salen)ONO_2]_2$ was dissolved in deuterated chloroform at −30 °C, the same NMR spectrum as that of a $Fe(salen)O_2NO$ solution at −30 °C was observed. These results indicated that low-magnetic-moment dimers do not exist in solution to any appreciable extent, even at low temperature.

Since mull infrared spectra of the solids in the 1200–1600-cm^{-1} region were useful in determining the bonding mode of the nitrate, organic solvents for the nitrate complexes were sought that had little or no absorption in that region. Infrared spectra of the complexes in these solvents would indicate the binding mode of the nitrate. Bromoform and methylene bromide were found to be suitable, and the solution infrared spectra of $[Fe(salen)ONO_2]_2$ and $Fe(salen)O_2NO$ in these solvents were identical in the region. Bands at 1530, 1250, and 1010 cm^{-1} were found and were indicative of the bidentate form in these solutions. KRS-5 solution cells were used for these measurements to prevent any possibility of anion exchange that might occur with NaCl or KBr cells.

Final Comments. Solid $Fe(salen)NO_3$ may occur either as a dimer with unidentate nitrate ligands or as a monomer with a bidentate nitrate. The dimer–monomer formation appears to be similar to that found with Fe(L)X complexes, which have unidentate anions, being controlled by solvent and the nature of the salicylideneamine. The bidentate nitrate complex is not unexpected since the $[Fe(salen)]^+$ unit is flexible and has been shown to bind with several bidentate ligands.[45,46,47] In solution, $Fe(salen)NO_3$ appears to be monomeric with a bidentate nitrate.

This study suggests that nitrate complexes of iron(III) macrocycles are able to form in organic solvents, even in the presence of water, when high concentrations of nitrate are available. Both iron and nitrate are found in a variety of materials, such as soil and biological systems.[48] It is possible that iron nitrate complexes may be present in these materials in aqueous and nonaqueous phases and may affect the properties of the materials.

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Registry No. Fe(salen)O_2NO, 97337-05-8; [Fe(salen)ONO_2]$_2$, 97337-06-9; [Fe(salpn)ONO_2]$_2$, 97337-07-0; [Fe(5-Clsalen)ONO_2]$_2$, 97337-08-1; [Fe(5-MeOsalen)ONO_2]$_2$, 97337-09-2; Fe(TPP)O_2NO, 76282-27-4; [Fe(salen)]$_2$O, 18601-34-8; [Fe(salpn)]$_2$O, 97337-10-5; [Fe(5-Clsalen)]$_2$O, 18601-71-3; [Fe(5-MeOsalen)]$_2$O, 97374-04-4; ^{15}N, 14390-96-6.

Supplementary Material Available: Figure S1, the Raman spectra of [Fe(salen)ONO_2]$_2$ and Fe(salen)O_2NO, and Table SI, magnetic data for Fe(salen)O_2NO and [Fe(salen)ONO_2]$_2$ at various temperatures (2 pages). Ordering information is given on any current masthead page.

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Polydentate Ligands Containing Phosphorus. 8. Coordination Complexes of a New Uninegative Tridentate Ligand, Tris(diphenylthiophosphinoyl)methanide, and Related Compounds and the Molecular Structure of (Bis(dimethylthiophosphinoyl)(diphenylthiophosphinoyl)methanido)chloromercury(II)[1]

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The reaction of mercury(II) chloride, bromide, or iodide in ethanol solution with tris(diphenylthiophosphinoyl)methane, $[(C_6H_5)_2P(S)]_3CH$, or bis(dimethylthiophosphinoyl)diphenylthiophosphinoylmethane, $[(CH_3)_2P(S)]_2[(C_6H_5)_2P(S)]CH$, yields coordination compounds of the type $\{[(C_6H_5)_2P(S)][R_2P(S)]_2C\}HgX$, where R is C_6H_5 or CH_3, and X is Cl, Br, or I. The X-ray crystallographic structural determination of (bis(dimethylthiophosphinoyl)(diphenylthiophosphinoyl)methanido)chloromercury(II), $\{[(CH_3)_2P(S)]_2[(C_6H_5)_2P(S)]C\}HgCl$ (monoclinic, $P2_1/a$, $Z = 4$, $a = 1.48$ (1) nm, $b = 1.394$ (9) nm, $c = 1.194$ (8) nm, and $\beta = 112.038$ (6)°), proves that the organophosphorus ligand coordinates to mercury in a tridentate fashion via the three sulfur atoms to form a cage compound of six-membered chelate rings. Chlorine occupies the fourth coordination position about the pseudotetrahedral mercury atom. Raman spectra of the solid coordination compounds $\{[R_2P(S)]_3C\}MX$, where M = Hg, Cd, indicate an unusually large decrease of the P–S stretching frequency compared to those of the neutral parent ligands. Phosphorus-31 NMR data are also reported for the complexes.

Introduction

The chemistry of phosphorus compounds that have three phosphorus atoms attached to the same carbon atom is relatively new. In 1966, Birum and Matthews[3] reported mesomeric ylide salts containing this atomic arrangement, and in 1970 Issleib and Abicht[4] reported the synthesis of the first analogue, tris(diphenylphosphino)methane, $(Ph_2P)_3CH$, and its trisulfide, $[Ph_2P(S)]_3CH$, of the compounds reported here. Additional analogues of these potential ligands have been synthesized and characterized recently.[5–11] However, very little coordination chemistry of these tris ligands[12] has been reported. Osborn[13,14] has reported on the behavior of $(Ph_2P)_3CH$, HTris,[12] as a tridentate ligand in nickel, iridium, and several other metal carbonyl clusters in which each phosphine is bonded to a different metal atom of a triangular face of the cluster. Likewise van Koten[15] has shown that one molecule of HTris can simultaneously bond to three silver atoms in a novel complex. Finally, we[9] have shown HTris can be bidentate in complexes of the group 6 metal carbonyls. In view of the large variety of potential ligands available in the new class of tris compounds, viz. $[R_2P(X)][R_2P(Y)][R_2P(Z)]CH$, where R = Ph, Me and X, Y, Z = electron pair, O, S, Se, and in view of the various polydentate and ambidentate bonding patterns possible, we have begun a systematic investigation of the coordination chemistry of these ligands. Further, removal of the methine proton of a tris(trichalcogenide) would generate an anion that is potentially tridentate, i.e., an anionic tripod ligand. The only precedent for a uninegative tridentate ligand is the well-known polypyrazolylborate[16,17] ligand system. It is therefore of great interest

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