

Ce(IV). After the evolution of N₂ was complete, the volume of the gas was measured.

Acknowledgment. This research was supported by the National Science Foundation through Grant MPS-75-08188.

Registry No. MoO(S₂CN(CH₃)₂)₂, 39587-09-2; MoO(S₂CN(CH₃)(C₆H₅CH₂)₂)₂, 65452-63-3; MoO(S₂CN(C₂H₅)₂)₂, 25395-92-0; MoO(S₂CN(*i*-C₃H₇)₂)₂, 65483-45-6; [(*n*-C₃H₇)₄N]N₃, 993-21-5; N₂, 7727-37-9; NH₃, 7664-41-7.

References and Notes

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Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Reaction of μ -Oxo-Bridged Iron(III) Complexes with Organic Acids: A Characterization of the Products

RONALD G. WOLLMANN and DAVID N. HENDRICKSON*¹

Received February 14, 1977

The products from the reactions of μ -oxo-bis(*N,N'*-ethylenebis(salicylideneiminato)iron(III)), [Fe(salen)]₂O, with trichloroacetic acid (tcaH), trifluoroacetic acid (tfaH), salicylic acid (salH), picric acid (picH), and picolinic acid (picH) are characterized. Dimeric compounds of composition [Fe(salen)X]₂ are obtained where X is tca⁻, tfa⁻, sal⁻, or pic⁻. A monomeric compound of composition Fe(salen)X is obtained when X is pico⁻. Monomeric compounds of composition Fe(TPP)(X) are obtained from the reaction of μ -oxo-bis(tetraphenylporphyrinato)iron(III), [Fe(TPP)]₂O, with picH and tcaH. An antiferromagnetic exchange interaction is indicated by variable-temperature (4.2–267 K) magnetic susceptibility data for the dimeric salen compounds. Exchange parameters, *J*, in the range of -4.5 to -7.0 cm⁻¹ are obtained for the dimers by least-squares fitting of the data to the theoretical equation for an isotropic exchange interaction ($\hat{H} = -JS_1 \cdot S_2$) for *S*₁ = *S*₂ = 5/2 with the inclusion of a monomeric ferric impurity. Iron-57 Mössbauer parameters are reported for Fe(salen)(pico) and [Fe(salen)(tfa)]₂. X-Band (8–300 K) and Q-band (100–300 K) EPR spectra are presented. Very complex EPR spectra at 90 K are obtained for the [Fe(salen)X]₂ compounds. No EPR signals are observed at 8 K for the dimeric compounds in the X-band spectra. Infrared spectra at ~30 and 300 K are reported. An absorption in the 850-cm⁻¹ region is observed for Fe(salen)(pico) as well as for each [Fe(salen)X]₂ compound. These absorptions are tentatively assigned to the asymmetric stretching vibration for the moiety



Introduction

The equilibria and reactions involved in the formation and dissociation of μ -oxo-bridged iron(III) complexes are known to be complicated and are not totally understood.^{2–6} Mechanisms have been proposed⁴ which involve various dimeric species such as di- μ -hydroxo-, μ -alkoxo- μ -hydroxo-, μ -halo- μ -hydroxo-, μ -aquo- μ -hydroxo-, and di- μ -halo-bridged iron(III) complexes. Several di- μ -alkoxo-^{7–10} and di- μ -hydroxo-bridged^{11,12} iron(III) dimers have been isolated and characterized.

Organic acids react with μ -oxo-bridged iron(III) complexes. In this paper we report the synthesis and characterization of the reaction products of several organic acids with μ -oxo-bis(tetraphenylporphyrinato)iron(III), [Fe(TPP)]₂O, and μ -oxo-bis(*N,N'*-ethylenebis(salicylideneiminato)iron(III)), [Fe(salen)]₂O.

Results and Discussion

The reaction of a CH₃Cl solution of [Fe(salen)]₂O with certain organic acids has been found to give compounds with the composition of Fe(salen)X, where X⁻ is variously the monoanion of trichloroacetic acid (tcaH), trifluoroacetic acid (tfaH), salicylic acid (salH), picric acid (picH), or picolinic acid (picoH). In the following sections it will be shown that, except for the picolinic acid compound, these compounds are dimers, [Fe(salen)X]₂. On the other hand, it will be shown that the similarly prepared Fe(TPP)X compounds, where X⁻ is the monoanion of trichloroacetic or picric acid, are probably monomeric.

Magnetic Susceptibility Measurements. Variable-temperature (4.2–270 K) magnetic susceptibility data were collected for the five Fe(salen)X compounds and also for

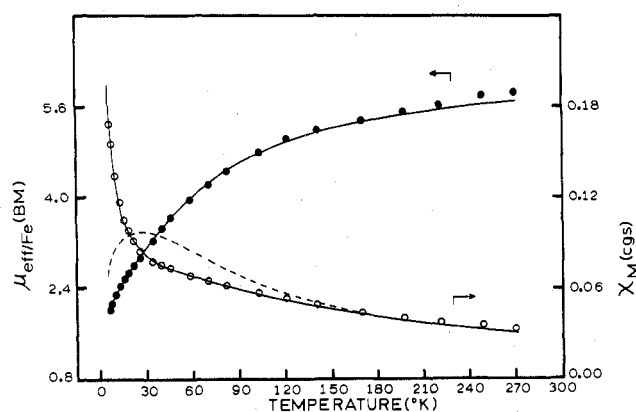


Figure 1. Molar paramagnetic susceptibility in cgsu and effective magnetic moment per iron in μ_B vs. temperature curves for $[\text{Fe}(\text{salen})(\text{tfa})]_2$. The solid lines result from least-squares fitting of the data to the $S_1 = S_2 = 5/2$ dimer equation including a paramagnetic impurity ($g = 2.0$, no TIP included). The dashed line results from fitting the susceptibility data without a paramagnetic impurity.

$\text{Fe}(\text{TPP})(\text{tca})$ and $\text{Fe}(\text{TPP})(\text{pic})$. The data appear as supplementary material. The room-temperature effective magnetic moments for all five salen compounds are in the range of 5.5–6.0 μ_B , which is obviously characteristic of high-spin iron(III) complexes. Three of the compounds, $\text{Fe}(\text{TPP})(\text{pic})$, $\text{Fe}(\text{TPP})(\text{tca})$, and $\text{Fe}(\text{salen})(\text{pico})$, exhibit magnetic susceptibility curves that are typical of monomeric high-spin iron(III) complexes. The effective magnetic moments of the latter two compounds are relatively constant down to temperatures of ~ 30 K, whereupon the effective moments decrease with further decrease in the temperature. Zero-field interactions arising from spin-orbit admixture of excited states into the ground state, and to a lesser degree intermolecular magnetic exchange interactions and magnetic Zeeman interactions, are responsible for the decrease in μ_{eff} below ~ 30 K. Zero-field splitting is greater for an iron(III) porphyrin as compared to the salen complex and, as such, μ_{eff} is 3.8 μ_B at 4.2 K for $\text{Fe}(\text{TPP})(\text{tca})$, whereas $\text{Fe}(\text{salen})(\text{pico})$ has $\mu_{\text{eff}} = 5.5 \mu_B$ at 4.2 K. The data for these three monomeric compounds were not fit to a theoretical model.

Antiferromagnetic exchange interactions are evident in the data for the other four $\text{Fe}(\text{salen})\text{X}$ compounds. With decreasing temperature, the μ_{eff} for each compound decreases from a value in the range of 5.5–6.0 μ_B per iron ion at room temperature to a value in the range of 0.7–1.4 μ_B per iron ion at 4.2 K. As a typical example, Figure 1 illustrates the magnetic susceptibility data for the trifluoroacetate compound. The data clearly indicate the presence of a dimeric association in this solid. This compound is best formulated, then, as $[\text{Fe}(\text{salen})(\text{tfa})]_2$, where there is a magnetic exchange between two high-spin iron(III) ions.

The magnetic exchange interaction in a ferric dimer can be treated with an isotropic spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, and perturbation theory. An equation for the molar paramagnetic susceptibility of an $S_1 = S_2 = 5/2$ exchange-coupled dimer has been presented.^{13–15} To this equation we added a term representing the paramagnetic susceptibility of a possible monomeric ferric impurity (χ_{para}) and this gives

$$\chi_M = \left(\frac{Ng^2\beta^2}{kT} \right) \frac{2A + 10B + 28C + 60D + 110E}{1 + 3A + 5B + 7C + 9D + 11E} + \frac{4.2}{T} \chi_{\text{para}}$$

In this expression N , g , β , k , and T have their usual meanings. The last term is constructed such that for a dimer with an appreciable exchange parameter the susceptibility at 4.2 K is assumed to be due only to the monomeric ferric impurity.

Table I. Parameters Obtained from Magnetic Susceptibility Fittings

	J , cm^{-1}	% Fe^{3+} impurity	CC ^a
$[\text{Fe}(\text{salen})(\text{pic})]_2$	-4.5 ± 0.5	3.2 ± 1.8	-0.52
$[\text{Fe}(\text{salen})(\text{tca})]_2$	-5.7 ± 0.4	3.5 ± 0.8	-0.22
$[\text{Fe}(\text{salen})(\text{tfa})]_2$	-6.3 ± 0.3	11 ± 2.0	-0.30
$[\text{Fe}(\text{salen})(\text{sal})]_2$	-7.0 ± 0.8	8.6 ± 2.0	-0.56

^a CC is the correlation coefficient between the exchange parameter and the % Fe^{3+} impurity parameter and is obtained from the fitting program.

The exponential terms are $A = \exp(2J/kT)$, $B = \exp(6J/kT)$, $C = \exp(12J/kT)$, $D = \exp(20J/kT)$, and $E = \exp(30J/kT)$.

A least-squares-fitting computer program was used to fit the data for $[\text{Fe}(\text{salen})(\text{tfa})]_2$ to the above equations. An isotropic g value of 2.0 was assumed and temperature-independent paramagnetism was neglected. This left two parameters: the exchange parameter, J , and the paramagnetic susceptibility of the impurity, χ_{para} . A least-squares fitting was carried out assuming that there was no monomeric iron(III) impurity, (i.e., $\chi_{\text{para}} = 0$). As can be seen in Figure 1 (dashed line), using only one parameter (J) gave a relatively poor fit, particularly to the data at low temperatures. This was also found to be characteristic of the data for the other three interacting $[\text{Fe}(\text{salen})\text{X}]_2$ compounds. When the fitting was carried out including a monomeric iron(III) impurity, an excellent fit to the data for $[\text{Fe}(\text{salen})(\text{tfa})]_2$ was obtained with $J = -6.3 \pm 0.3 \text{ cm}^{-1}$ and $11 \pm 2.0\%$ by weight of a monomeric iron(III) impurity. The solid lines in Figure 1 illustrate this fit.

Similar fits were obtained for the other compounds. The fitting parameters are summarized in Table I. The least-squares fittings indicate substantial monomeric impurities in the tfa^- and sal^- compounds, which will be discussed in a later section. It is important to know how much the J values resulting from these fittings are influenced by the incorporation of the second parameter, the percentage of monomeric iron(III) impurity. Correlation coefficients between the two fitting parameters for each compound are given in Table I and they range from -0.2 to -0.6 . Correlation coefficients of this magnitude are indicative of some degree of interdependence of the parameters during the minimization process. The model of iron(III) dimers with some monomeric iron(III) impurities does fit the data quite well with J values in the range of -4.5 to -7.0 cm^{-1} for the four $[\text{Fe}(\text{salen})\text{X}]_2$ compounds.

The magnitude of the J values could give some insight into the nature of the dimeric association. It is quite obvious that the four $[\text{Fe}(\text{salen})\text{X}]_2$ compounds do *not* have μ -oxo bridges, for μ -oxo-bridged iron(III) dimers have J values of approximately -100 cm^{-1} .¹⁴ Compounds such as $[\text{Fe}(\text{salen})\text{Cl}]_2$ are known^{16,17} to be dimeric by virtue of an association of two square-pyramidal $\text{Fe}(\text{salen})\text{Cl}$ moieties with their basal planes facing each other. One of the two salen phenoxide oxygen atoms from each $\text{Fe}(\text{salen})\text{Cl}$ moiety interacts with the other iron ion. Exchange parameters in the range of -6 to -8 cm^{-1} have been reported¹⁸ for $[\text{Fe}(\text{salen})\text{Cl}]_2$ and analogous compounds and, as such, this type of dimeric association is a distinct possibility for our four $[\text{Fe}(\text{salen})\text{X}]_2$ compounds. Also, di- μ -hydroxo- and di- μ -alkoxo-diiron(III) compounds are known to have J values in the -8 to -17 cm^{-1} range.^{8,9,12} It is, thus, also possible that the four $[\text{Fe}(\text{salen})\text{X}]_2$ compounds are bridged by two oxygen atoms, one from each of the X^- species. It does not seem likely that the complexes are, in fact, di- μ -hydroxo bridged. In this case, the clear indication of high-spin $\text{Fe}(\text{III})$ from the room-temperature susceptibilities would mean that XH , not X^- , is present.

Electron Paramagnetic Resonance Measurements. X-Band EPR measurements were carried out at 300, 90, and 8 K and Q-band measurements at 300 and 90 K for all compounds.

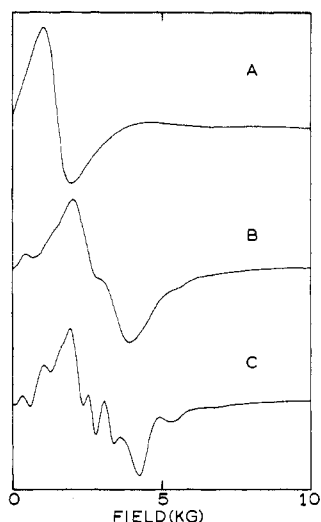


Figure 2. The 90 K X-band EPR spectra of solid samples of (A) Fe(salen)(pico), (B) [Fe(salen)(tfa)]₂, and (C) [Fe(salen)(sal)]₂.

No signals were observed for X-band frequencies at 300 K for Fe(TPP)(tca), Fe(TPP)(pic), or Fe(salen)(pico) or for any of the dimeric [Fe(salen)X]₂ compounds. Relatively strong X-band signals were observed at 90 K, whereas weak or no signals were observed at 8 K. Strong signals were observed at both room-temperature and near-liquid-nitrogen temperature for each of the compounds using Q-band frequencies.

A broad derivative at $g = 4.3$ was observed in the X-band spectra for Fe(salen)(pico) at both 90 and 8 K. The same broad feature was also present in the Q-band at 300 and 90 K. Many monomeric high-spin iron(III) complexes with zero-field splittings greater than the EPR microwave energies ($> \sim 0.3 \text{ cm}^{-1}$ for X-band) show a $g = 4.3$ signal associated with the perpendicular transition in the $M_S = \pm 1/2$ Kramers doublet.¹⁹ The simple $g = 4.3$ signal is indicative of the monomeric nature of Fe(salen)(pico).

Figure 2 gives a comparison of the 90 K X-band spectrum (tracing A) of monomeric Fe(salen)(pico) with the 77 K spectra of two of the exchange-interacting dimers, [Fe(salen)(tfa)]₂ (tracing B) and [Fe(salen)(sal)]₂ (tracing C). The 90 K X-band spectra for the analogous tca⁻ and pic⁻ compounds are similar to the tfa⁻ spectrum in Figure 2. It can be seen that the four [Fe(salen)X]₂ dimers have EPR spectra that appear to be considerably more complicated than the spectrum for the pico⁻ compound. This is to be expected. The exchange parameters for the [Fe(salen)X]₂ compounds appreciably exceed the EPR microwave energies that were used (~ 0.3 and $\sim 1.2 \text{ cm}^{-1}$). These molecules effectively have dimer electronic states with a total spin S' of 5, 4, 3, 2, 1, and 0, with the singlet ($S' = 0$) state at lowest energy. The singlet state does not give rise to an EPR signal, but EPR signals would be expected for the other states. The signals would be complicated by single-ion and dipolar zero-field interactions. The complexity of the EPR spectra observed for the [Fe(salen)X]₂ compounds does support the suggestion that there are dimers in the solid. Decreasing the temperature of these samples leads to a loss of the 90 K signals to give a very weak $g \approx 4.2$ signal. At 8 K, essentially only the dimer $S' = 0$ state is thermally populated, and the $g \approx 4.2$ signals observed at this temperature are clear indicators of monomeric iron(III) impurities in agreement with the analysis of the susceptibility data.

Two other observations were made on the [Fe(salen)X]₂ compounds with EPR measurements. First, Figure 3 illustrates the 90 K Q-band EPR spectrum of a powdered sample of [Fe(salen)(sal)]₂, which shows that at $\sim 35 \text{ GHz}$ this compound exhibits a multitude of EPR transitions. The Q-band

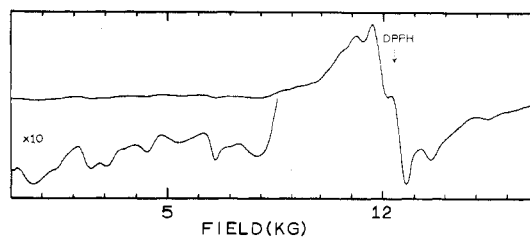


Figure 3. The 100 K Q-band EPR spectrum of a solid sample of [Fe(salen)(sal)]₂.

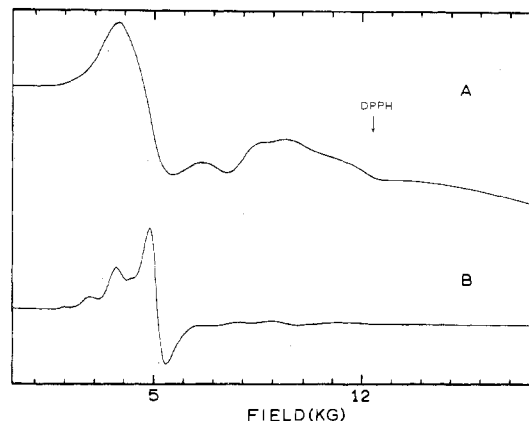


Figure 4. Q-Band EPR spectra of a solid sample of Fe(TPP)(tca) at (A) 300 K and (B) 100 K.

spectra for the other three dimers are also rich with features. Second, X-band spectra at 90 K were also obtained for 1:1 DMF/CHCl₃ and 1:1:3 propionitrile/ethanol/diethyl ether glasses of the four [Fe(salen)X]₂ compounds. In each case, a strong $g \approx 4.2$ signal and a very weak $g = 8.0$ signal were observed. This indicates that in solution the dimeric association is *not* maintained. Conductivity measurements on Fe(salen)(pico) and [Fe(salen)(tca)]₂ in absolute ethanol as a function of concentration indicated that both compounds are 1:1 electrolytes. Of the two possible modes of dimer bridging mentioned in the last section, it seems that the type present in [Fe(salen)Cl]₂ would be more susceptible to dissociation in solution.

The 90 K X-band EPR spectrum of Fe(TPP)(tca) consists of a broad (half-width at half-maximum of 680 G) signal at $g = 5.6$ and a broad shouldering feature at $g \approx 2.9$. No X-band signal was observed at 8 K. Two resolved signals at $g = 5.4$ and $g = 3.4$ were seen in the room-temperature Q-band spectrum. Lowering the temperature to 100 K resolved the $g = 5.4$ signal into several peaks which result from zero-field interactions. This temperature dependence is shown in Figure 4.

The 90 K X-band spectrum of Fe(TPP)(pic) showed a broad $g = 5.31$ and weak $g = 2.07$ and 1.99 signals. Only a very weak $g = 5.80$ signal was observed at 8 K. The room-temperature Q-band spectrum consisted of signals at $g = 6.51$, 3.64 , and 2.03 . At 100 K, the spectrum signals were seen at $g = 5.35$, 4.16 , and 2.04 . For both Fe(TPP)(X) compounds, the observed EPR spectra are very characteristic of monomeric high-spin iron(III) porphyrins.

Iron-57 Mössbauer Spectra. ⁵⁷Fe Mössbauer spectra were obtained at 90 K for dimeric [Fe(salen)(tfa)]₂ and monomeric Fe(salen)(pico). In both cases, the spectra consisted of a single quadrupole-split doublet. The doublets were fit to Lorentzian curves with reasonable line widths. There was no indication of an impurity doublet. Fitting the doublet for the tfa⁻ compound gave an isomer shift of $0.411 (1) \text{ mm/s}$ relative to iron metal and a quadrupole splitting of $1.397 (1) \text{ mm/s}$. The doublet for the pico⁻ compound gave an isomer shift and

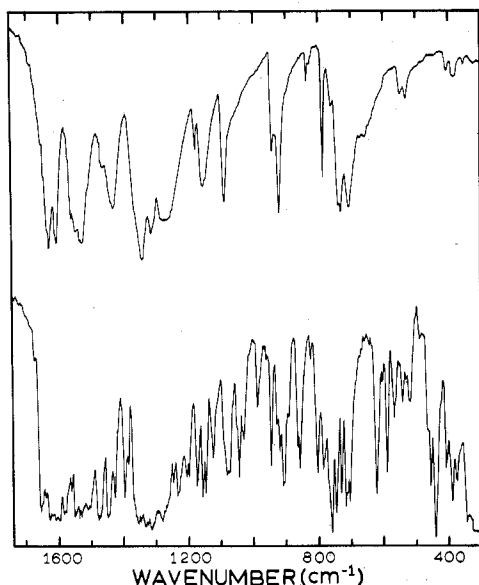


Figure 5. Room-temperature IR spectrum of picric acid (top) and ~ 30 K IR spectrum of $[\text{Fe}(\text{salen})(\text{pic})]_2$ (bottom).

quadrupole splitting of 0.537 (1) and 0.913 (1) mm/s, respectively. *Dimeric* $[\text{Fe}(\text{salen})\text{Cl}]_2$ and $[\text{Fe}(\text{salen})\text{Br}]_2$ have been reported to have quadrupole splittings of 1.45 and 1.63 mm/s, respectively. *Monomeric* solvated adducts of $[\text{Fe}(\text{salen})\text{Cl}]$ have been reported to have splittings in the range of 0.87–1.6 mm/s.²⁰ Only one Mössbauer spectrum has been reported for a di- μ -alkoxo-bridged iron(III) compound with a quadrupole splitting of 1.00 mm/s.⁷ The isomer shifts that have been reported for these three types of Schiff base iron(III) compounds fall in the range of 0.33–0.50 mm/s and are not characteristic of the structural type.

The quadrupole splitting for $[\text{Fe}(\text{salen})(\text{tfa})]_2$ is close to that reported for $[\text{Fe}(\text{salen})\text{Cl}]_2$ and this could point to a similar dimeric association in the two solids. However, the overlapping range of quadrupole splittings reported for the monomeric $[\text{Fe}(\text{salen})\text{Cl}]$ species makes a differentiation of structural characteristics less definitive.

Infrared Spectra. KBr-pellet IR spectra were run for each of the salen compounds both at room temperature and at ~ 30 K (improved resolution). The ~ 30 K spectrum for $[\text{Fe}(\text{salen})(\text{pic})]_2$ and the room-temperature spectrum for picric acid are given in Figure 5. Previous infrared work with alkoxo-bridged iron(III) complexes has led to an assignment of several transitions in the 300–600-cm⁻¹ region as Fe–O vibrations.^{8,21} A characteristic strong absorption at ~ 1050 cm⁻¹ was also observed. On the other hand, the $[\text{Fe}(\text{salen})\text{Cl}]_2$ -type compounds exhibit a band at ~ 850 cm⁻¹, which has been assigned as a stretching band for the moiety²⁰



Each of our $[\text{Fe}(\text{salen})\text{X}]_2$ compounds do have a medium-intensity band in the 840–870-cm⁻¹ region. As can be seen in Figure 5, $[\text{Fe}(\text{salen})(\text{pic})]_2$ has a band at 860 cm⁻¹, while picric acid clearly does not have an absorption in this region. The presence of this band for each of our exchange-interacting compounds supports the suggestion that these compounds have the $[\text{Fe}(\text{salen})\text{Cl}]_2$ structure. However, some of the free organic acids have absorptions in the 850-cm⁻¹ region, thus preventing a definitive structural assignment in all cases.

Magnetic susceptibility and EPR data indicated that $[\text{Fe}(\text{salen})(\text{pico})]$ is monomeric; that is, there is not an appreciable exchange interaction. As illustrated in Figure 6, the ~ 30 K

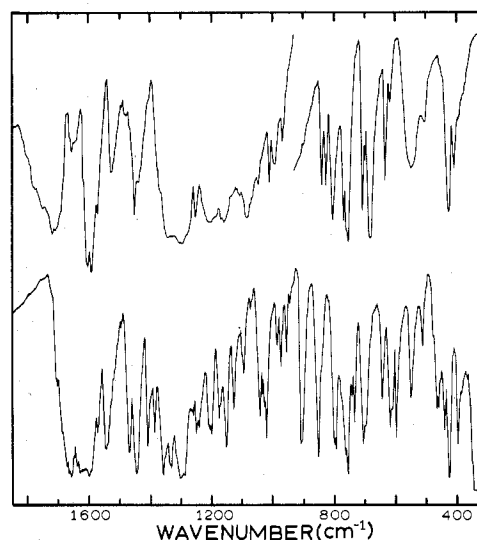


Figure 6. Room-temperature IR spectrum of picolinic acid (top) and ~ 30 K IR spectrum of $[\text{Fe}(\text{salen})(\text{pico})]$ (bottom).

IR spectrum of this compound does show a relatively intense absorption at 852 cm⁻¹ which is not found in the picolinic acid spectrum. If $[\text{Fe}(\text{salen})(\text{pico})]$ does have *basically the same* structure as the exchange-interacting compounds, it is difficult to give a detailed explanation without structural work of why there is no magnetic exchange. It is possible that the organic acid anions in the interacting $[\text{Fe}(\text{salen})\text{X}]_2$ compounds are bound to the iron ions with carboxylate oxygen atoms, whereas in $[\text{Fe}(\text{salen})(\text{pico})]$ the pico⁻ moiety binds to each iron ion with the ring nitrogen atom. If the dimeric association is weaker in this compound, this would explain the apparent absence of an exchange interaction.

Conclusion

The reaction of organic acids with $[\text{Fe}(\text{salen})]_2\text{O}$ has been shown to give dimeric and exchange-interacting $[\text{Fe}(\text{salen})\text{X}]_2$ compounds when the acid (X^- is conjugate base) is trichloroacetic, trifluoroacetic, salicylic, or picric acid. With picolinic acid an apparently monomeric compound, $[\text{Fe}(\text{salen})(\text{pico})]$, results. The dimeric association in the four $[\text{Fe}(\text{salen})\text{X}]_2$ compounds is probably similar to that found for $[\text{Fe}(\text{salen})\text{Cl}]_2$. The reaction of $[\text{Fe}(\text{TPP})]_2\text{O}$ with trichloroacetic and picric acids has been shown to give monomeric high-spin $[\text{Fe}(\text{TPP})(\text{tca})]$ and $[\text{Fe}(\text{TPP})(\text{pic})]$.

Experimental Section

Compound Preparation. Samples of $[\text{Fe}(\text{salen})]_2\text{O}$ and $[\text{Fe}(\text{TPP})]_2\text{O}$ were prepared as described previously.²² Essentially the same procedure was followed in the reaction of $[\text{Fe}(\text{salen})]_2\text{O}$ with either trichloroacetic acid, trifluoroacetic acid, salicylic acid, picric acid, or picolinic acid. In general, $[\text{Fe}(\text{salen})]_2\text{O}$ (0.5 g) was dissolved in ~ 60 mL of CHCl_3 . The solid organic acid in excess of 1:3 molar ratio was added to the solution. In the case of trifluoroacetic acid, 15 drops of the acid was added. In all cases, the solution was stirred for approximately 5 min during which time the solid $[\text{Fe}(\text{salen})]_2\text{O}$ dissolved to give a dark red solution. The solution was slowly filtered into ~ 175 mL of diethyl ether with vigorous stirring. The resulting dark reddish black solid was collected by filtration, washed with ether, and dried in vacuo over P_2O_{10} . The solid that was obtained with salicylic acid required recrystallization from CHCl_3 . The trifluoroacetate compound required thorough washing with diethyl ether in order to obtain an analytically pure compound. Anal. Calcd for $[\text{Fe}(\text{salen})(\text{tca})]_2$, $\text{C}_{36}\text{H}_{28}\text{N}_4\text{Fe}_2\text{O}_8\text{Cl}_6$: C, 44.62; H, 2.92; N, 5.78; Fe, 11.53. Found: C, 44.09; H, 2.86; N, 5.65; Fe, 11.34. Calcd for $[\text{Fe}(\text{salen})(\text{tfa})]_2$, $\text{C}_{36}\text{H}_{28}\text{N}_4\text{Fe}_2\text{O}_8\text{F}_6$: C, 49.68; H, 3.25; N, 6.44; Fe, 12.83. Found: C, 49.66; H, 3.40; N, 6.60; Fe, 12.57. Calcd for $[\text{Fe}(\text{salen})(\text{sal})]_2$, $\text{C}_{46}\text{H}_{38}\text{N}_4\text{Fe}_2\text{O}_{10}$: C, 60.14; H, 4.18; N, 6.10; Fe, 12.16. Found: C, 59.40; H, 4.05; N, 5.92; Fe, 11.67. Calcd for $[\text{Fe}(\text{salen})(\text{pic})]_2$, $\text{C}_{44}\text{H}_{32}\text{N}_{10}\text{Fe}_2\text{O}_{18}$: C, 48.02; H, 2.94; N, 12.73;

Fe, 10.15. Found: C, 47.81; H, 3.13; N, 12.51; Fe, 9.93. Calcd for Fe(salen)(pico), $C_{22}H_{18}N_3FeO_4$: C, 59.47; H, 4.09; N, 9.46; Fe, 12.57. Found: C, 58.16; H, 4.13; N, 9.47; Fe, 12.08.

The reactions of trichloroacetic acid and picric acid with $[Fe(TPP)]_2O$ followed similar procedures. $[Fe(TPP)]_2O$ was dissolved in chloroform and the solution brought to reflux. A large excess of trichloroacetic acid in water or picric acid in 95% ethanol was added to the solution with stirring. The solution was stirred at reflux for 15–30 min and then evaporated to about half of the original volume. Several 15-mL aliquots of H_2O were used to wash the chloroform solution. The solution was then evaporated to give the desired compound. Anal. Calcd for Fe(TPP)(tca), $C_{46}H_{28}N_4FeO_2Cl_3$: C, 66.48; H, 3.40; N, 6.74; Fe, 6.72. Found: C, 64.79; H, 3.46; N, 6.44; Fe, 6.45. Calcd for Fe(TPP)(pic), $C_{50}H_{28}N_7FeO_7$: C, 67.12; H, 3.16; N, 10.96; Fe, 6.24. Found: C, 65.74; H, 3.64; N, 10.59; Fe, 5.99.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. Samples were prepared as 13-mm KBr pellets. Low-temperature IR spectra were obtained using a Cryogenics Technology, Inc., "Spectrim" closed-cycle helium gas refrigerator with the cryocooling head equipped with KBr windows (50×4 mm).

Variable-temperature (4.2–269 K) magnetic susceptibility data were obtained with a PAR Model 150A vibrating-sample magnetometer. The temperature was monitored with a GaAs temperature-sensitive diode in conjunction with a $CuSO_4 \cdot 5H_2O$ standard.

Electron paramagnetic resonance spectra were obtained with Varian E-line spectrometers using an E101 microwave bridge with a 6-in. (10 kG) magnet for X-band measurements and an E110 microwave bridge with a 12-in. (25 kG) magnet for Q-band measurements. A Varian liquid-nitrogen X-band cavity insert was used to obtain measurements at 90 ± 10 K and an Air Products Heli-tran X-band liquid-helium cooling system to obtain measurements at 8 ± 2 K. Temperatures for the X-band measurements were determined by employing an Ohmite carbon resistor ($2.7 \pm 10\%$ k Ω , $1/8$ W). The low-temperature Q-band measurements were estimated to be at ~ 100 K and were obtained by surrounding the cavity with a glass Dewar and passing liquid-nitrogen-cooled, gaseous nitrogen through the system.

Iron-57 Mössbauer measurements at 90 K were obtained on an instrument which was referred to in an earlier paper.²²

Computer fittings of the magnetic susceptibility data were performed with an adapted version of the minimization program known as STEPT.²³ Computer fittings of the ^{57}Fe Mössbauer data were performed with a modified version of a previously described program.²⁴

Acknowledgment. We thank Professor P. G. Debrunner and Mr. C. R. Hill for assistance with the ^{57}Fe Mössbauer work.

We are grateful for partial funding for our work from National Institutes of Health Grant HL 13652.

Registry No. $[Fe(salen)(tca)]_2$, 47892-68-2; $[Fe(salen)(tfa)]_2$, 24932-25-0; $[Fe(salen)(sal)]_2$, 65466-06-0; $[Fe(salen)(pic)]_2$, 65516-32-7; Fe(salen)(pico), 65466-05-9; Fe(TPP)(tca), 65466-04-8; Fe(TPP)(pic), 65466-03-7; $[Fe(salen)]_2O$, 18601-34-8; $[Fe(TPP)]_2O$, 12582-61-5; picric acid, 88-89-1; picolinic acid, 98-98-6.

Supplementary Material Available: Tables II–VIII giving magnetic susceptibility data (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Substituent and Solvent Effects on the Electrochemical Properties of Tetra- μ -carboxylato-dirhodium(II)

K. DAS, K. M. KADISH,* and J. L. BEAR*

Received July 28, 1977

The electrochemical oxidation–reduction of tetra- μ -carboxylato-dirhodium(II), $Rh_2(O_2CR)_4$, where $R = (CH_3)_3C$, C_3H_9 , C_3H_7 , C_2H_5 , CH_3 , $C_6H_5CH_2$, CH_3OCH_2 , $C_6H_5OCH_2$, CH_3CHCl , and CF_3 was investigated by polarography, cyclic voltammetry, and controlled potential electrolysis. At a platinum electrode $Rh_2(O_2CR)_4$ was reversibly oxidized by a single electron to yield a stable Rh(II)–Rh(III) dimer. The same compound was irreversibly reduced in several steps but yielded initially a Rh(II)–Rh(I) dimer before further addition of one or more electrons. The half-wave potentials were found to depend on the nature of the substituent R and also the solvent. The polar substituent constants of Taft were found to bear a linear relationship with the half-wave potentials, and for a particular complex, the solvent dependency of its $E_{1/2}$ values was shown to be roughly related to the solvent donor number.

For the past few years, we have been investigating the biological activity of several tetra- μ -carboxylato-dirhodium(II) complexes.^{1–3} These complexes are potent inhibitors of enzymes which have sulfhydryl groups near or at the active site.⁴

Reaction of most sulfhydryl containing compounds with tetra- μ -carboxylato-dirhodium(II) is rapid at mid or high pH and results in a release of the carboxylate ions from the "cage" complex. The product has a complicated EPR spectra and