Inorganica Chimica Acta, *112* (1986) 23–27

The Reaction of Amines with N,N′-ethylenebis(salicylideneiminato)(nitrato)iron(III) and Related Complexes

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Received May 23, 1985

Abstract

The title compound, Fe(salen)NO_3, was reacted with imidazole, 1-methylimidazole, piperidine, and morpholine in either chloroform or dichloromethane solution. The reactions were monitored with proton NMR and electronic spectra and conductance measurements. The imidazole bases appeared to react with the complex in a 2:1 fashion with displacement of the nitrate, producing a high-spin iron(III) complex. The secondary amines promoted hydrolysis with any trace water present to form $[Fe(salen)]_2O$. The chloro complex, Fe(salen)Cl, did not react with the imidazole bases, but did form the μ-oxo complex when a large excess of piperidine was present. The N,N′-phenylenebis-(salicylideneimine) complex, Fe(salphen)NO_3, was found to precipitate from an imidazole (im) chloroform solution as the high-spin complex, Fe(salphen)NO_3·2im.

Introduction**

The complex, Fe(salen)NO_3, has recently been prepared and studied in the solid and solution satc [1]. While investigating the nature of this complex in solution, it was noted that the nitrate ion was relatively easily displaced from the $Fe(salen)^+$ group by organic bases, such as imidazole (im) and 1-methylimidazole (N-Meim), especially when compared to the Cl^- ion displacement from Fe(salen)Cl. Little work has been reported on the base adducts formed with $Fe(salen)^+$ and the nitrate substitution method provided a way to examine them.

In this report, proton NMR and electronic spectral data and conductance data on the reaction of Fe(salen)NO_3 and Fe(salen)Cl with im, N-Meim, piperidine (pip) and morpholine (mor) are presented. Investigations of the reaction of pip with Fe(TPP)Cl have shown that autoreduction takes place producing Fe(TPP)·2pip, an Fe(II) complex [2], and we wished to see if such a reaction would occur with the $Fe(salen)^+$ complexes. Also, Fe(salphen)NO_3 was considered in this study in order to determine if the structural change from an ethyleneimine bridge in $Fe(salen)^+$ to the aromatic *o*-phenyleneimine one in $Fe(salphen)^+$ would affect the results.

Experimental

Materials

Fe(salen)NO_3 [1] and Fe(salen)Cl [3] were prepared by literature procedures and were shown to exhibit the proper visible and proton NMR spectra. Both compounds in the solid state appeared to be in the dimeric form as shown by infrared spectra [4].

Fe(salphen)NO_3 was prepared by the same procedure that was used to prepare other iron(III) salicylideneimine nitrate complexes [1]. It had the following properties: mass spectrum, 50 eV, m/e (relative intensity) 432(55), 386(27), 370(100); IR (mull) nitrate bands 1480, 1280, 1000, dimer bands 870, 850 cm^{-1}; electronic spectrum λ_{max} (log ϵ_{max}) 413sh(3.9), 361sh(4.1), 328 nm(4.29); magnetic data (room temperature) χ_m(corr) 0.0113 cgs units, 5.2μ_β, diamagnetic correction -310×10^{-6}. *Anal.* Calc. for $C_{20}H_{14}N_3O_5Fe$: N, 9.72; Fe, 12.92. Found: N, 9.44; Fe, 12.13%.

The infrared spectrum of Fe(salphen)NO_3 in bromoform solution showed bands at 1535 and 1250 cm^{-1}, instead of 1480 and 1280 cm^{-1}, indicating the presence of the monomeric, bidentate nitrate in solution [1].

Dichloromethane and chloroform were dried immediately prior to use following standard procedures [5]. Deuterated solvents (Aldrich Chemical Co.) were used as received. The amines, except for mor, were newly purchased (Aldrich Chemical Co.) and were used as received, except for the addition of molecular sieves to N-Meim and pip. Morpholine was distilled prior to use and stored

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**Abbreviations: im, imidazole; mor, morpholine; N-Meim, 1-methylimidazole; PPN^+Cl^-, bis-(triphenylphosphoranylidene)ammonium chloride; salen, N,N′-ethylenebis-(salicylideneimine)dianion; salphen, N,N′-phenylenebis-(salicylideneimine) dianion; TPP, *meso*-tetraphenylporphyrin dianion; pip, piperidine.

0020-1693/86/$3.50

over sieves. PPN^+Cl^- was obtained from Aldrich Chemical Co. and recrystallized from water..

Instrumentation

Conductance measurements were performed at room temperature using a YSI Model 32 conductance bridge with a Beckman pipet cell (cell constant = 0.100). All other instruments used have been described recently [1].

Measurements

The proton NMR measurements, made at probe temperature, were carried out using a 0.010 M iron complex dissolved in the deuterated solvent. Spectra were taken after adding incremental microgram amounts of the liquid amines or milligram amounts of the solid amine (im). The chemical shift values for $Fe(salen)NO_3$ have an uncertainty of approximately ±1 ppm.

For the conductance measurements a 0.002 M iron complex solution in dichloromethane was used, incremental amounts of a 0.002 M amine solution added, and the conductances measured. Each molar conductance, Λ_m, was calculated, using a dilution correction [6], and was able to be reproduced within five percent.

A 7.0×10^{-4} M iron complex solution in dichloromethane was prepared and incremental amounts of a 7.0×10^{-4} M amine solution and pure solvent were added to produce an iron complex concentration of 1.0×10^{-4}M. The spectra were measured from 700 to 250 nm.

When im was added to a 0.01 M $Fe(salphen)NO_3$ dissolved in chloroform, a black precipitate resulted which appeared to be $Fe(salphen)NO_3 \cdot 2im$. *Anal. Calc. for* $C_{28}H_{22}N_7O_5Fe$: N, 17.25; Fe, 9.83. Found: N, 16.68; Fe, 9.56%. It had a magnetic moment of 5.5 μ_β at room temperature. The addition of im to $Fe(salen)NO_3$ dissolved in chloroform produced a black solid with the following analyses: N, 15.82; Fe, 10.96%.

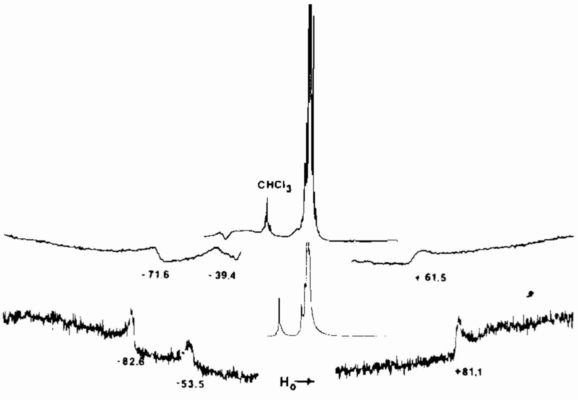

Fig. 1. Proton NMR spectra of (bottom) 0.01 M $Fe(salen)NO_3$ in $CDCl_3$ and (top) with 0.030 M N-Meim present, 30°, taken at 90 MHz. Spectra have different ppm scales.

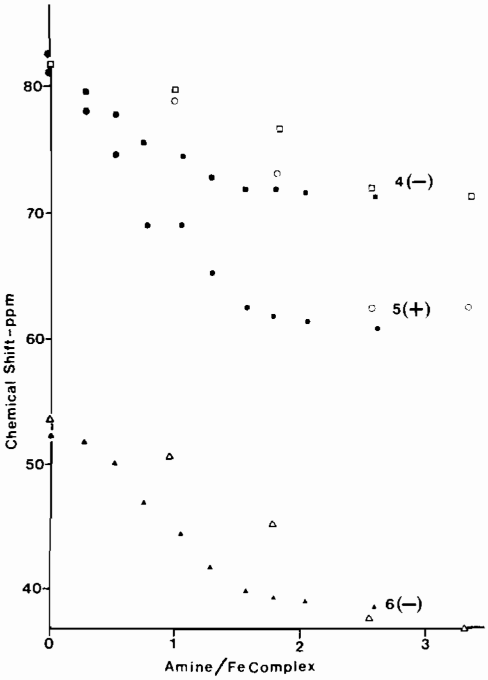

Fig. 2. Proton NMR chemical shifts *vs.* amine/$Fe(salen)NO_3$ ratio for salen protons. Closed symbols are for N-Meim addition in $CDCl_3$ and open symbols for im addition in CD_2Cl_2. Number at right indicates proton position on ring and sign in parentheses is the sign of the chemical shift.

Results

The dichloromethane and chloroform solutions of the high spin $Fe(salen)NO_3$ had the expected proton NMR spectra [1, 7], showing an alternating shift pattern for the phenyl resonances (Fig. 1). When im or N-Meim was added to the solutions, the downfield peaks (4-H and 6-H) shifted upfield, while the upfield peak (5-H) shifted downfield (Fig. 1 and Table I). (The upfield 3-H peak was not often observed.) The limiting proton signal values, reached when an excess of amine was present, were still within the range found for high-spin Fe(salen)X complexes (Table I). No spectral peaks due to low-spin complexes were observed. A graph (Fig. 2) of the resonance values *vs.* the base/complex ratio showed a rather sharp change as the ratio increased, with the limiting resonance value being reached at an approximate ratio of two. A comparison of the plots for the N-Meim and im additions indicated that for the N-Meim case, the limiting resonance values, which were the same for both amines, were reached at a slightly lower ratio than for the im case. The addition of the same bases to Fe(salen)Cl solutions

TABLE I. Proton NMR Spectral Data for Fe(salen)X and Fe(salphen)X Complexes[a]

X	Solvent	T (°C)	Peak assignments (δ)				Reference
			3-H	4-H	5-H	6-H	
For Fe(salen)X							
Cl	$CDCl_3$	27°	+84	−80	+70	−50	7
Cl	$CDCl_3$	30	+83	−78.3	+68.9	−49.3	
OAc	$CDCl_3$	27	+83	−78	+69	−48	16
OBz	$CDCl_3$	27	+84	−79	+70	−48	7
DBcatH	$CDCl_3$	amb	–	−71	+54	−42	17
NO_3	$CDCl_3$	30	+96	−82.6	+81.1	−53.5	1
NO_3	CD_2Cl_2	30	–	−81.7	+81.1	−52.7	
NO_3/im(10)[b]	CD_2Cl_2	30	–	−71.1	+62.3	−37.0	
NO_3/N-Meim(2.6)	$CDCl_3$	30	–	−71.4	+61.8	−39.0	
Cl/im(4.6)	CD_2Cl_2	30	–	−72.4	+60.3	−40.0	
Cl/N-Meim(2.1)	$CDCl_3$	30	–	−75.8	+65.7	−46.6	
			Peak assignments (δ)				
			4-H	5-H	6-H	phenyl	
For Fe(salphen)X							
NO_3	$CDCl_3$	30	−87.8	+82.8	−55.9	−27.8	
NO_3/N-Meim(2.5)	$CDCl_3$	30	−70	+59	–	−26	

[a] Abbreviations: DBcatH, 3,5-di-tert-butylcatechol anion; OBz, benzoate; OAc, acetate. See text for other abbreviations. [b] Number in parentheses is ratio of base to complex in solution.

showed only slight shifts in the resonance values (Table I) with no limiting values being reached, even when the base/complex ratio was greater than two.

The addition of N-Meim to a solution of Fe(salphen)NO_3 resulted in a proton NMR spectrum with broad peaks having peak centers that were difficult to determine precisely. However, the observed shifts did seem larger than those found for the Fe(salen)NO_3/N-Meim interaction. Adding im to a chloroform solution of Fe(salphen)NO_3 resulted in a solid which appeared to be Fe(salphen)NO_3·2im, a high-spin iron(III) complex. A solid with an uncertain nature resulted when im was added to a chloroform solution of Fe(salen)NO_3. Solids did not result in dichloromethane; therefore, this solvent was used for most of the measurements.

Room temperature conductance data in dichloromethane for the 0.001 M iron complex solutions with added amine were obtained. The following Λ_m values at an amine/iron ratio of two were obtained: N-Meim/Fe(salphen)NO_3, 20.1; N-Meim/Fe(salen)NO_3, 15.5; im/Fe(salen)NO_3, 4.5; and N-Meim/Fe(salen)Cl, 0.4 ohm^{-1} cm^2 mol^{-1}. Addition of N-Meim to a Fe(salphen)NO_3 solution produced a relatively large increase in Λ_m, while a similar addition to the Fe(salen)NO_3 produced a smaller effect. The addition of im to a Fe(salen)NO_3 solution gave only a relatively small change in Λ_m. When N-Meim was added to a 0.001 M Fe(salen)Cl solution little change in conductance was observed.

The electronic spectra of 1×10^{-4} M Fe(salen)NO_3 solutions were obtained with added im and N-Meim. Only small changes in the spectra were observed after adding the bases. The solution spectra with either excess (amine/complex ratio equal to four) im or N-Meim present were identical. Compared to the original Fe(salen)NO_3 spectrum the spectra of solutions with excess amine showed a small red shift (~10 nm) of the 525 nm band and about a ten percent decrease in intensity. No change in the spectrum of Fe(salen)Cl was observed when either N-Meim or im were added.

The proton NMR spectrum of 0.01 M Fe(salen)NO_3 in deuterochloroform changed markedly when pip was added incrementally, producing the spectrum of $[Fe(salen)]_2O$. When the pip concentration reached 5×10^{-3} M all of the high-spin complex spectrum was gone. Carrying the reaction out in oxygen-saturated solutions led to the same results. Morpholine required a higher concentration (11×10^{-3} M) to produce a complete disappearance of the Fe(salen)NO_3 spectrum. The addition of water to the Fe(salen)NO_3 solution did not produce the μ-oxo spectrum, but when pip was added evidence for the μ-oxo complex was immediately observed and a smaller concentration of pip was required to destroy the high-spin complex.

A 0.010 M Fe(salen)Cl solution showed the same behavior with pip, but a much higher concentration (0.020 M) was necessary to have only the μ-oxo complex present. No species other than the high-spin complex and the μ-oxo species were observed.

There was little or no change in the conductance of the Fe(salen)NO_3 solution as the secondary amines were added. However, the visible spectrum of Fe(salen)NO_3 was converted to that of the μ-oxo complex.

Discussion

The NMR spectral shifts observed as the imidazole amines were added to the Fe(salen)NO_3 solutions point to a maximum interaction ratio of two amines to one complex, with no low-spin Fe(III) adduct being formed. Displacement of the nitrate ion from the coordination sphere of the Fe is indicated by the conductance increase. However, a Λ_m value of 67.4 ohm^{-1} cm^2 mol^{-1}, shown by a 0.001 M PPN^+Cl^- solution, was not reached, even when the N-Meim/Fe(salphen)NO_3 ratio was 4.0 (Λ_m = 38.5 ohm^{-1} cm^2 mol^{-1}). Weak association of the ion with the product complex may keep the conductance lower than expected. The greater NMR spectral and conductance changes shown by the Fe(salphen)NO_3 solution compared to those of Fe(salen)NO_3 does indicate a structural effect.

A question that we wished to answer in this study was: does the addition of the first amine (B) produce a loss of nitrate or not? The equations representing this are:

$$\mathrm{Fe(salen)NO_3 + B} = \left[\begin{array}{c}\mathrm{Fe(salen)(NO_3)\,(B)} \\ \text{or} \\ \mathrm{Fe(salen)(B)^+ + NO_3^-}\end{array}\right]$$

$$\overset{+B}{=} \mathrm{Fe(salen)B_2^+ + NO_3^-}$$

Since five-coordinate Fe(salen)X complexes are relatively common and since considerable rearrangement has to occur to form the observed six-coordinate *β-cis* salen structure [8, 9], it would have been of interest to have some evidence on the nature of the monoamine complex. Unfortunately the conductance measurements did not show if the nitrate was lost in the first step or not. Attempts to calculate formation constants for the amine complexes, using spectral and conductance data were fruitless. Considering the changes in the solution properties of the Fe(III) complexes as bases were added, the formation constants are probably small for the nitrate complexes, but are essentially zero for the chloride complex. Unlike the iron(III) porphyrins [10–12] there is little tendency for the iron(III) salicylideneimines to bind N-Meim and im.

A reviewer pointed out an article by Nishida *et al.* [13] in which the ESR spectra of the six-coordinate low-spin Fe(III) complexes, Na[Fe(salen)$(CN)_2$] and the bis-im adduct of the complex involving the 3-methoxysalen derivative were examined. These complexes had different ESR spectra than those of related porphyrin complexes and the differences were ascribed to a different electronic structure of the ground states produced by weaker axial interaction for the Schiff base complexes. It is interesting to note that the addition of a methoxy group to the 3-position of each phenyl ring of the salen ligand is enough to produce a low-spin complex when im is added.

Hydrolysis of Fe(salen)NO_3 with the trace water present appears to be promoted by pip,

$$\mathrm{Pip + H_2O = pipH^+ + OH^-}$$

$$\mathrm{2Fe(salen)NO_3 + 2OH^-}$$

$$\mathrm{= [Fe(salen)]_2O + H_2O + 2NO_3^-}$$

The reaction is strongly dependent on the base strength of the secondary amine since mor(pK_b 5.67), a weaker base than pip(pK_b 2.88), required a greater concentration of base to effect the complete formation of the μ-oxo complex. The reaction produced no low-spin iron(II) complexes, ruling out the possibility of autoreduction. Comparing the Fe(II)/Fe(III) half-wave potentials of $Fe(TPP)^+$ complexes with those of $Fe(salen)^+$, for example, Fe(TPP)N_3 ($E_{1/2}$ = –0.25 V) [14] and Fe(salen)N_3 ($E_{1/2}$ = –0.62 V) [15], both in dimethylformamide, indicate that reduction of $Fe(TPP)^+$ is more easily accomplished than that for the $Fe(salen)^+$ unit.

Acknowledgement

This investigation was supported by PHS Grant Number 1RO1CA35733-01, awarded by the National Cancer Institute, DHHS.

References

1 J. C. Fanning, J. L. Resce, G. C. Lickfield and M. E. Kotun, *Inorg. Chem., 24,* 2884 (1985).
2 J. DelGaudio and G. N. LaMar, *J. Am. Chem. Soc., 100,* 1112 (1978).
3 M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A:,* 1900 (1967).
4 R. G. Wollmann and D. N. Hendrickson, *Inorg. Chem., 17,* 926 (1978).

5 A. J. Gordon and R. A. Ford, 'The Chemist's Companion', Wiley, New York, 1972, p. 430.

6 D. T. Sawyer, W. R. Heineman and J. M. Beebe, 'Chemistry Experiments for Instrumental Methods', Wiley, New York, 1984, p. 63.

7 R. H. Heistand II, R. B. Lauffer, E. Fikrig and L. Que Jr., *J. Am. Chem. Soc., 104,* 2789 (1982).

8 R. B. Lauffer, R. H. Heistand II and L. Que Jr., *Inorg. Chem., 22,* 50 (1983).

9 M. Nakamura, T. Itoh, H. Okawa and S. Kida, *J. Inorg. Nucl. Chem., 43,* 2281 (1981).

10 G. N. LaMar and F. A. Walker, in D. Dolphin (ed.), 'The Porphyrins, Vol. IV, Part B', Academic Press, New York, 1978, p. 61.

11 M. M. Doeff and D. A. Sweigert, *Inorg. Chem., 21,* 3699 (1983).

12 G. A. Tondreau and D. A. Sweigert, *Inorg. Chem., 23,* 1060 (1984).

13 Y. Nishida, S. Oshio and S. Kida, *Inorg. Chim. Acta, 23,* 59 (1977).

14 L. A. Bottomley and K. M. Kadish, *Inorg. Chem., 20,* 1348 (1981).

15 A. Puxxedo and G. Costa, *J. Chem. Soc. Dalton Trans.,* 2327 (1977).

16 G. N. LaMar, G. R. Eaton, R. H. Holm and F. A. Walker, *J. Am. Chem. Soc., 95,* 63 (1973).

17 R. B. Lauffer, R. H. Heistand II and L. Que Jr., *J. Am. Chem. Soc., 103,* 3947 (1981).