The Characterization of Oligomeric Iron(II)-tetraoxime Complexes

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(Received September 29, 1971)

Several polymeric iron(II) chelates with tetraoxime ligands,

$$CH_3C(NOH)C(NOH)\text{-}\overset{(\alpha)}{CH_2}\text{-}\overset{(\beta)}{CH_2}\text{-}(CH_2)_n\text{-}\overset{(\beta)}{CH_2}\text{-}\overset{(\alpha)}{CH_2}\text{-}C(NOH)C(NOH)CH_3,$$

where $n=2$ and 6, were characterized. They show a ligand-to-iron molar ratio of 1:1, corresponding to a planar arrangement of the ferrous ion and the four oxime nitrogens; two pyridine or methylpyridine substituents are axially coordinated to the central metal ion. The complexes are diamagnetic in the solid state, and their absorption spectra closely resemble those of the monomeric ferrous dimethylglyoxime compounds. The molecular weight, determined in a pyridine solution by vapor-pressure osmometry (2800 for $-(CH_2)_2-$ and 3100 for $-(CH_2)_6-$), corresponds to 5 or 6 $Fe–N_4$ units within the polymer chain. An NMR investigation including tetraoxime ligands with both aliphatic and aromatic linkages, as well as the corresponding chelates, shows that the protons in the α or in the β position to the oxime groups do not undergo any shift upon chelation. The electronic spectral data and NMR data provide no evidence that the Fe(II) chelate rings within the polymer chain are affected by one another.

In a recent work,[1] polymeric ferrous tetraoxime complexes with aromatic groups as linkage between the two α-dioxime ligand units have been synthesized and characterized. In the present study, two low-molecular-weight ferrous tetraoxime polymers with methylene bridges, $-(CH_2)_6-$ and $-(CH_2)_{10}-$, will be described. The molecular model shows that, because of the extended methylene chain, the α-dioxime groups are situated at random in space, this results in a structure far less rigid than the one incorporating phenyl- or similar bridging groups. An NMR study shows that the chelation of the oxime nitrogens does not cause any shift to the protons adjacent to the chelate ring. The polymer chain is thus considered to be formed of $Fe–N_4$ units independent of one another.

The properties and the structures of these new chelates are compared with those of the monomeric iron(II)-α-dioxime complexes, as well as with those of the previously-reported polymeric chelates.

Experimental

Preparation of the Tetraoxime Ligands. Dodecane-2,3,10,11-tetraone-tetraoxime, and hexadecane-2,3,14,15-tetraone-tetraoxime were prepared according to the methods described by Murahashi and Kubota.[2] The products obtained showed the following characteristics.

Dodecane-2,3,10,11-tetraone-tetraoxime. White crystals; soluble in DMSO, DMF, pyridine, and other organic solvents; mp 251—253°C. (Found: C, 50.41; H, 7.61; N, 19.33%.)

Hexadecane-2,3,14,15-tetraone-tetraoxime. White crystals; soluble in DMSO, DMF, and pyridine; insoluble in ethanol, methanol, *etc.*; mp 240—241°C. (Found: C, 56.18; H, 8.72; N, 16.28%.)

Preparation of the Complexes. One millimole of an iron(II) salt (Mohr's salt) was dissolved under nitrogen in 20 m*l* of water; to this solution we then added, at room temperature, a solution of 0.5 mmol of a tetraoxime ligand in 5 m*l* of the base (pyridine, methylpyridine). An intensely-red-colored precipitate immediately formed. The reaction mixture was stirred for five hours. The product was then filtered, washed extensively with water and ethanol, and then dried *in vacuo* at room temperature.

The red powders obtained were all soluble in pyridine. They were only slightly soluble in other organic bases and were extremely unstable in common organic solvents (DMF, DMSO, *etc.*). The yield was quantitative. The analytical data are shown in Table 1.

Apparatus and Procedures. The molecular weight was determined in a pyridine solution at 25°C, using a Mechrolab vapor-pressure osmometer, Model 302.

Table 1. Analytical data of the polymeric iron(II)-complexes with tetraoximes, $CH_3\text{-}C(NOH)\text{-}C(NOH)\text{-}(CH_2)_n\text{-}C(NOH)\text{-}C(NOH)\text{-}CH_3$;[a] $n=6$, 10

Compound number		Dissociation temp. (°C)[b]	Found, %				Calcd, %			
			C	H	N	Py	C	H	N	Py
1	$(CH_2)_6TOH_2\cdot Fe\cdot (Py)_2$[c]	190	52.20	5.97	16.06	29.85	53.01	6.06	16.86	31.74
2	$(CH_2)_6TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$[c]	165	52.68	6.13	14.96		54.75	6.51	15.96	
3	$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$[c]	160	53.28	6.22	15.26		54.25	6.51	15.96	
4	$(CH_2)_{10}TOH_2\cdot Fe\cdot (Py)_2$	195	56.10	7.01	14.93	27.93	56.31	6.90	15.15	28.53
5	$(CH_2)_{10}TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$	160	56.39	7.16	14.21		57.73	7.26	14.42	
6	$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	165	56.37	7.51	13.82		57.73	7.26	14.42	

a) Tetraoximes will be abbreviated as $(CH_2)_n$ TOH_4.
b) Temperature at which the compounds turn black without melting.
c) "Py," "β-Pic," and "γ-Pic" stand for pyridine, β-picoline, and γ-picoline respectively.

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[1] J. Backes, I. Masuda, and K. Shinra, This Bulletin, **45**, 1061 (1972).

[2] S. Murahashi and H. Kubota, *ibid.*, **35**, 1465 (1962).

The NMR spectra were obtained with a Japan Electron Optics JNM-3H-60 spectrometer at 60 Mc/sec, using tetramethylsilane as the internal reference. Under a nitrogen atmosphere, equimolar amounts of the tetraoxime ligand and an iron(II) salt were dissolved in 1 m*l* of deuterated pyridine; the solution was kept at room temperature for 5 hours before recording. We used solutions of 10% for the ligands and up to 20% for the ferrous complexes. The addition of D_2O caused the disappearance of the oxime protons of the free ligands at a low field.

The apparatus and techniques concerning the infrared and electronic spectra, the thermogravimetric analyses, and the magnetic properties have been described previously.[1]

Results and Discussion

Table 1 shows the anlytical data of the different chelate polymers. They indicate a tetraoxime ligand-to-iron molar ratio of 1: 1, and thus a structure where two α-dioxime groups and the ferrous ion form a planar arrangement and where the pyridine ligands (pyridine and methylpyridine) are axially substituted. This structure is further supported by the following thermogravimetric and spectral data.

The thermogravimetric curve (*cf.* Fig. 1) shows the characteristic pattern expected for the release of two coordinated pyridine molecules. The weight loss observed (29.9%) is in fair agreement with the calculated value (31.7%).

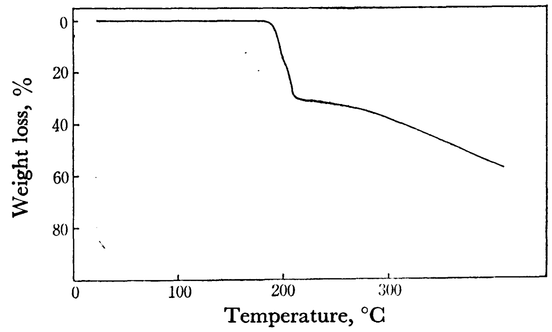

Fig. 1. Thermogravimetric analysis of $(CH_2)_6TOH_2\cdot Fe\cdot (Py)_2$ under nitrogen atmosphere.

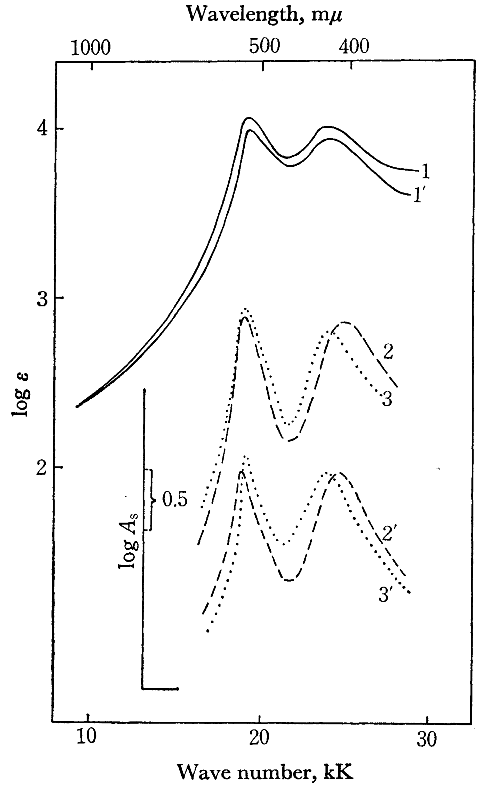

Fig. 2. Absorption spectra: 1: $(CH_2)_{10}TOH_2\cdot Fe\cdot (Py)_2$ in pyridine; 2: $(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$ in γ-picoline;*) 3: $(CH_2)_{10}TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$ in β-picoline;*) 1': $(CH_2)_6TOH_2\cdot Fe\cdot (Py)_2$ in pyridine; 2': $(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$ in γ-picoline;*) 3': $(CH_2)_6TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$ in β-picoline.*)

*) Concentration inaccurate due to low solubility.

While, for the tetraoxime polymers with aromatic linkages, no pyridine and pyridine-like bases were found to be axially coordinated in the solid state,[1] the present polymers readily underwent this axial substitution.

The polymers are soluble in pyridine. The absorp-

TABLE 2. ELECTRONIC ABSORPTION SPECTRA

Complexes	ν_{max}, kK (log ε)		Solvents
$(CH_2)_6TOH_2\cdot Fe\cdot (Py)_2$	19.4 (4.00)	24.5 (3.95)	Py
$(CH_2)_6TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$	19.4	24.5	Py
$(CH_2)_6TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$	19.3	24.1	β-Pic
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	19.3	24.2	Py
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	19.1	24.7	γ-Pic
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	18.7		Aniline
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	18.6		Hydrazine Hydrate
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	17.9		Ethylenediamine
$(CH_2)_6TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	17.9		Piperidine
$(CH_2)_{10}TOH_2\cdot Fe\cdot (Py)_2$	19.4 (4.06)	24.0 (4.00)	Py
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$	19.3	24.0	Py
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\beta\text{-Pic})_2$	19.3	24.0	β-Pic
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	19.3	24.2	Py
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	19.0	24.8	γ-Pic
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	18.7		Aniline
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	18.6		Hydrazine Hydrate
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	17.9		Piperidine
$(CH_2)_{10}TOH_2\cdot Fe\cdot (\gamma\text{-Pic})_2$	17.7		Ethylenediamine

Table 3. Comparision of the charge-transfer bands in the monomeric and the polymeric ferrous chelates

Complexes	Fe→Py CT	Fe→Oxime CT
$(DmgH)_2 \cdot Fe \cdot (Py)_2$[4]	26.0 (kK)	19.6 (kK)
$(CH_2)_6TOH_2 \cdot Fe \cdot (Py)_2$	24.5	19.4
$(CH_2)_{10}TOH_2 \cdot Fe \cdot (Py)_2$	24.0	19.4
$(BzdH)_2 \cdot Fe \cdot (Py)_2$[a),6]	25.7	18.3(18.6,sh)
$(FrdH)_2 \cdot Fe \cdot (Py)_2$[a),6]	25.7	17.6(19.2,sh)
$(C_6H_4\text{-}O\text{-}C_6H_4)TOH_2 \cdot Fe(Py)_2$[1]	25.0	18.5
$(C_6H_4\text{-}C_6H_4)TOH_2 \cdot Fe \cdot (Py)_2$[1]	25.6	18.3
$(2,6\text{-Pyridyl})TOH_2 \cdot Fe \cdot (Py)_2$[1]	24.8(27.5,sh)	18.4

a) BzdH and FrdH represent monoanions of α-benzildioxime and α-furildioxime respectively.

b) 'sh' stands for shoulder.

tion spectra in a pyridine solution (*cf.* Fig. 2) bear a close resemblance to those of the monomeric ferrous dimethylglyoxime compounds, $(DmgH)_2 \cdot Fe \cdot (Py)_2$, for which two intense absorption bands are found at 19.6 and 26.0 kK; they are assigned to the Fe→oxime and the Fe→pyridine charge transfers respectively.[3,4,5] The absorption bands of the tetraoxime complexes with axial pyridine are found in the same region (*cf.* Table 3). In monomeric ferrous complexes involving aromatic dioxime ligands (*i.e.*, α-benzil-dioxime or α-furil-dioxime), as well as in the polymeric chelates with aromatic bridges, the Fe→oxime charge-transfer bands undergo almost the same shifts as the dimethylglyoxime compounds (Table 3). The fact that no considerable shifts occur upon the linking together of several of these $Fe\text{–}N_4$ units indicates further that the different chelate rings within the polymer chain are independent of one another and that the iron(II) $d\pi$-electrons do not engage into an extended π-delocalization in the case of aromatic linkage groups. The effect of substitution on the axially-coordinated pyridine is the same in the monomeric as in the polymeric compounds (*cf.* Table 2 and Ref. 4). The electronic states of the ferrous ion in the monomer and in the polymer may thus be considered to be quite similar.

The absorption spectra at different pH values, ranging ftom pH 8.9 to pH 4.9 fail to show one single isosbestic point; this indicates a two-step dissociation of the axial base. A look at the thermogravimetric curve supports this assumption.

The ferrous tetraoxime compounds with aromatic linkages were all paramagnetic in the solid state. Upon dissolution in pyridine, these compounds are considered to undergo spin-pairing to form octahedrally-substituted diamagnetic complexes.[1] The present tetraoxime chelates with axial pyridine substituents were all found to have negative susceptibilities at room temperature in the solid state; this indicates a low-spin ferrous ion in the complexes. This is consistent with the high extinction coefficient of the absorption bands in the visible region (Fig. 2).[3]

The infrared spectra of the ligands exhibit a broad absorption band between 1620 and 1680 cm^{-1}. Upon coordination with iron(II), a strong band appears in

Table 4. NMR spectral data[a)] of the bis(α-ketoxime) ligands, $CH_3C(NOH)CO\text{-}R\text{-}COC(NOH)CH_3$ and $CH_3COC(NOH)CH_2\text{-}R'\text{-}CH_2C(NOH)COCH_3$

Compound	Chemical shift, τ CH_3	CH_2	$CH_2\text{-}C{=}N$	Ring -CH=		=N-OH	Solvent
R:							
$C_6H_4\text{-}O\text{-}C_6H_4$	7.96			2.85	2.06	−2.37	$(CD_3)_2SO$
	(s, 6H)			(d, 4H, *J*: 9 cps)	(d, 4H, *J*: 9 cps)	(s, 2H)	
	7.58			2.91	1.73	−4.55	C_5D_5N
	(s, 6H)			(d, 4H, *J*: 9 cps)	(d, 4H, *J*: 9 cps)	(s, br, 2H)	
$C_6H_4\text{-}C_6H_4$	7.92			2.11		−2.46	$(CD_3)_2SO$
	(s, 6H)			(m, 8H)		(s, 2H)	
	7.55			2.34	1.75	−4.73	C_5D_5N
	(s, 6H)			(d, 4H, *J*: 8.75 cps)	(d, 4H, *J*:8.75 cps)	(s, 2H)	
R′:							
$(CH_2)_4$	7.68	8.74	7.6[b)]			−2.21	$(CD_3)_2SO$
	(s, 6H)	(m, 8H)				(s, 2H)	
	7.52	8.53	7.2			−4.40	C_5D_5N
	(s, 6H)	(m, 8H)	(m, br, 4H)			(s, 2H)	
$(CH_2)_8$	7.70	8.78	7.5[b)]			−2.20	$(CD_3)_2SO$
	(s, 6H)	(m, 16H)				(s, 2H)	
	7.50	8.75	7.1			−4.45	C_5D_5N
	(s, 6H)	(m, 16H)	(m, br, 4H)			(s, br, 2H)	

a) Parts per million downfield from tetramethylsilane; s=singlet, d=doublet, m=multiplet, br=broad.

b) Overlap with $(CD_3)_2SO$.

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[3] M. J. Cowan, J. M. F. Drake, and R. J. P. Williams, *Discuss. Faraday Soc.*, **27**, 217 (1959), and the references cited therein.

[4] Y. Yamano, I. Masuda, and K. Shinra, This Bulletin, **44**, 1581 (1971).

[5] The *d-d* bands of low-spin ferrous dimethylglyoxime complexs with axially-coordinated bases are predicted in a region between 15 and 25 kK, but they are believed to be obscured by the intense charge-transfer bands in the visible region (G. De Alti, V. Galasso, A. Bigotto, and G. Costa, *Inorg. Chim. Acta*, **3**, 533 (1969); the *d-d* bands of pyridine-substituted ferrous dimethylglyoxime complexes in ethanol could only be detected in the case of axial 3-methyl-pyridine at 14.0 and 15.4 kK ($\log \varepsilon = 2.0$ and 2.16 respectively) (Ref. 4). In the present ferrous tetraoxime complexes, no *d-d* bands were detected.

[6] T. Matsumoto, Y. Yamano, and K. Shinra, *Nippon Kagaku Zasshi*, **89**, 44 (1968).

TABLE 5. NMR SPECTRAL DATA[a)] OF THE TETRAOXIME LIGANDS AND THEIR FERROUS POLYMER COMPLEXES, $CH_3C(NOH)C(NOH)$-R-$C(NOH)C(NOH)CH_3$ and $CH_3C(NOH)C(NOH)CH_2$-R′-$CH_2C(NOH)C(NOH)CH_3$

Compound	Chemical shift, τ CH_3	CH_2	CH_2–C=N	Ring –CH=		=N–OH		Solvent
R:								
C_6H_4-O-C_6H_4 Ligand	7.95 (s, 6H)			3.05 (d, 4H, *J*: 9 cps)	2.80 (d, 4H, *J*: 9 cps)	−1.44 (s, 4H)		$(CD_3)_2SO$
	7.38 (s, 6H)			2.81 (d, 4H, *J*: 9 cps)	2.28 (d, 4H,*J*: 9 cps)	−3.50 (s, 2H)	−3.80 (s, 2H)	C_5D_5N
	7.52 (s, 6H)			2.90 (d, 4H, *J*: 9 cps)	2.48 (d, 4H, *J*:9 cps)			$C_5D_5N/CDCl_3$ (1:1)
Complex	7.38 (s, 6H)			2.81 (d, br, 4H, *J*:9 cps)	2.28 (d, br, 4H, *J*:9 cps)			C_5D_5N
C_6H_4-C_6H_4 Ligand	7.88 (s, 6H)			2.73 (d, 4H, *J*:8.75 cps)	2.35 (d, 4H, *J*: 8.75 cps)	−1.55 (s, 4H)		$(CD_3)_2SO$
	7.32 (s, 6H)			2.12 (s, br, 8H)		−3.57 (s,2H)	−3.86 (s, 2H)	C_5D_5N
Complex	7.33 (s, 6H)			2.15 (s, br, 8H)				C_5D_5N
R′:								
$(CH_2)_4$ Ligand	8.04 (s, 6H)	8.70 (m, 8H)	7.5[b)]			−1.26 (s, 2H)	−1.34 (s, 2H)	$(CD_3)_2SO$
	7.51 (s, 6H)	8.35 (m, 8H)	6.85 (m, br, 4H)			−3.45 (s, 4H)		C_5D_5N
Complex	7.52 (s, 6H)	8.35 (m, 8H)	6.88 (m, br, 4H)					C_5D_5N
$(CH_2)_8$ Ligand	8.07 (s, 6H)	8.73 (m, 16H)	7.5[b)]			−1.29 (s, 2H)	−1.36 (s, 2H)	$(CD_3)_2SO$
	7.47 (s, 6H)	8.73 (m, 16H)	6.82 (m, br, 4H)			−3.49 (s, 4H)		C_5D_5N
Complex	7.48 (s, 6H)	8.73 (m, 16H)	6.83 (m, br, 4H)					C_5D_5N

a), b): see Table 4.

the 1620 cm^{-1} region; its position changes only slightly from one chelate to another. This band is attributed to the C=N stretching mode within the chelate. In both the free ligands and the chelate compounds, the OH stretching vibrations are found around 3200 cm^{-1} indicating the presence of free end-group oximes in the latter.

The solubility of these ferrous tetraoxime polymers in pyridine permitted vapor-pressure osmometry measurements. For the chelates with $-(CH_2)_6-$, the molecular weight values were found at 2800 ± 50, and for the chelates with $-(CH_2)_{10}-$, at 3100 ± 50, thus indicating a chain-length of 5 to 6 units.

For neither of the coordination compounds could an X-ray diffraction pattern, indicating an inherent crystalline structure, be found; this is in agreement with the polymeric character of the complexes.

NMR Spectra. This investigation was carried out in order to determine whether the complexing of the four oxime nitrogens with a ferrous ion had an effect on the protons close to this chelate ring.

Compounds involving keto-oxime groups have been the subject of extensive NMR studies[7,8] because of their properties to form *syn-anti* isomers. In the case of α-ketoximes, several isomeric structures can be theoretically conceived; this number increases considerably when the tetraoxime compounds are considered. However, the results obtained for the present compounds show no evidence of the presence of different isomers.

The spectral data of the bis(α-ketoxime) compounds incorporating aromatic as well as methylene linkages are shown in Table 4. They are taken as a basis for assigning the protons in the tetraoxime compounds. The protons of the aromatic rings appear as two doublets in the region between 1 and 3 ppm (τ-scale); this pattern is characteristic of a *para*-substituted species.

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[7] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, (1969), p. 266, and the references cited therein.

[8] M. Tanaka, T. Shono, and K. Shinra, *Anal. Chim. Acta*, **46**, 125 (1969).

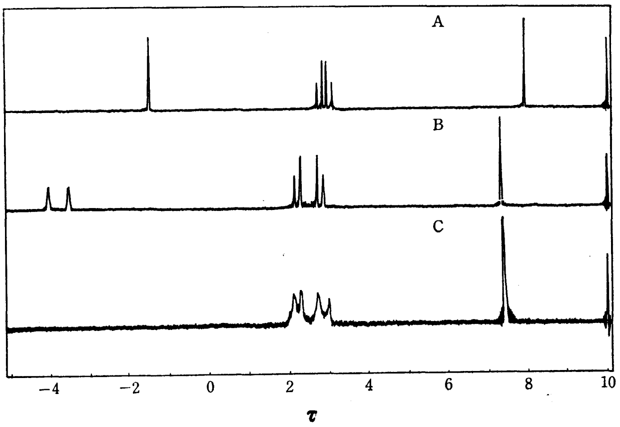

Fig. 3. NMR spectra.
A: C_6H_4-O-$C_6H_4TOH_4$ in $(CD_3)_2SO$
B: C_6H_4-O-$C_6H_4TOH_4$ in C_5D_5N
C: C_6H_4-O-$C_6H_4TOH_2\cdot Fe$ in C_5D_5N.

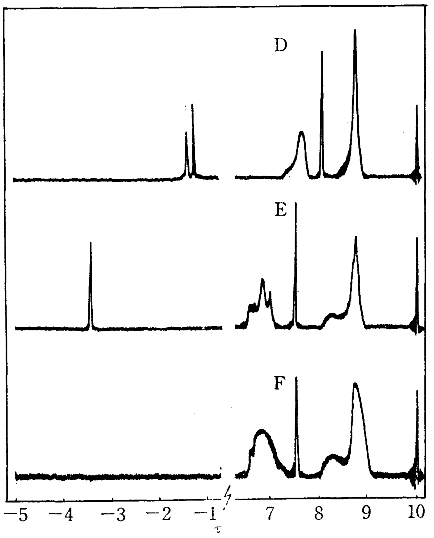

Fig. 4. NMR spectra.
D: $(CH_2)_{10}TOH_4$ in $(CD_3)_2SO$
E: $(CH_2)_{10}TOH_4$ in C_5D_5N
F: $(CH_2)_{10}TOH_2\cdot Fe$ in C_5D_5N

The oxime protons are found as sharp signals at a low field in DMSO; they are shifted to a lower field in pyridine. Through all of these spectra a common effect of the pyridine solvent is found, as all the signals undergo a shift, varying from 0.5 to 2.5 ppm toward a lower field than in the case of the spectra in DMSO. Further, the oxime protons appear as very sharp signals in DMSO, while in a pyridine solution the shape changes and the intensity decreases considerably.

The bis(α-ketoxime) compounds with methylene linkages show a broad absorption of the protons in the chain, extending over 1 ppm. The protons in the position α to the oxime C=N bond are shifted to a lower field. The oxime protons are found in the same region as those of the ketoximes with aromatic links. A similar solvent effect due to pyridine can be seen.

The spectra of the tetraoxime ligands are quite similar to those of the α-ketoxime compounds (*cf.* Table 5). The methyl protons appear as one sharp singlet (*cf.* Figs. 3 and 4). The oxime protons are found at a higher field than the monoxime compounds and appear either as a sharp singlet or as two less intense singlets, the latter at a lower field, in DMSO and in pyridine respectively.

Upon chelation in a pyridine solution, the position of neither the methyl protons nor the aromatic protons is altered (*cf.* Fig. 3); only the resolution decreases, and the oxime protons cannot be detected any more down to −20 ppm. For a series of monomeric Co(III) dimethylglyoxime compounds, the hydrogen-bond protons have been found to range between −8.1 and −8.5 ppm, depending on the nature of the complex.[9]

For the methylene-bridged tetraoxime chelate compounds, a similar spectral pattern is found (*cf.* Fig. 4). The positions of neither the methyl nor the methylene protons changes, while the oxime protons are no more detected down to −20 ppm.

The conclusion which can be drawn from these NMR data is that the protons in the α or in the β position relative to the oxime groups remain unaffected upon chelation with iron(II). Thus, no indication is found for an extended π-delocalization within the polymer chain involving the Fe(II)-*dπ* electrons.

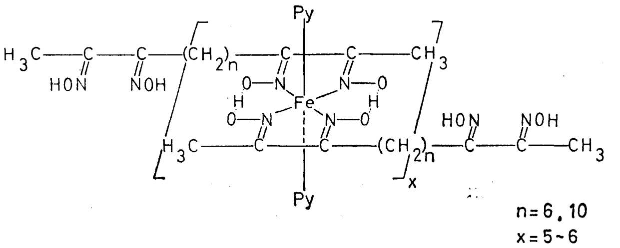

Fig. 5. Schematic representation of the pyridine-substituted, ferrous, methylene-bridged tetraoxime polymers.

Murahashi and Kubota[3] have suggested linear and cyclic structures for the nickel chelates of methylene- and phenyl-bridged tetraoximes. In a previous work we proposed a linear structure for the ferrous polymer chelates with aromatic linkages. This structure has been confirmed for the present methylene-bridged compounds (*cf.* Fig. 5). The infrared data as well as the molecular-weight data make it possible to eliminate the cyclic structures postulated by the above authors.

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[9] Y. Yamano, I. Masuda, and K. Shinra, *J. Inorg. Nucl. Chem.*, **33**, 521 (1970).