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Preparation and Properties of Iron(II) Complexes with Tetraoxime Analogues[1]

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Three polymeric iron(II)-tetraoxime chelates of the formula $CH_3C(NOH)C(NOH)\text{-}R\text{-}C(NOH)C(NOH)\text{-}CH_3$, where R: $C_6H_4\text{-}O\text{-}C_6H_4$, $C_6H_4\text{-}C_6H_4$, and 2,6-pyridyl, are characterized and compared with monomeric α-dioxime analogues. Analytical data indicate that in the solid state these $Fe\text{-}N_4$ type chelates do not coordinate an axial base. Axial substitution takes place only upon dissolution into pyridine or similar basic solvents. The resemblance between the substituted polymer chelates and the monomeric dimethylglyoxime compounds, as far as their electronic spectra are concerned, is discussed. While the solid state polymers are all paramagnetic with moments 2.0—2.5 B.M., ESR data show that in solution a conversion into a diamagnetic species takes place. A strong absorption band due to the O–N stretching vibration appears at about 1650 cm^{-1} upon complexing of the nitrogen atoms. The paramagnetism and the reflectance spectra of the solid state samples are related to their structure.

Many works have been presented dealing with the formation and properties of metal chelate polymers.[2] In these works the low solubility of the compounds often rendered a more accurate research impossible. Better understanding of the effect of polymerization on the central metal ion is expected from a further investigation of these chelate compounds.

Tetraoxime coordination polymers with nickel(II) and with cobalt(II), nickel(II), and copper(II) have been reported by Jones *et al.*[3] and Murahashi and Kubota,[4] respectively.

The present work involves an investigation of iron(II) complexes with ligands of the formula $CH_3C(NOH)C(NOH)\text{-}R\text{-}C(NOH)C(NOH)CH_3$, where R stands for $C_6H_4\text{-}O\text{-}C_6H_4$, $C_6H_4\text{-}C_6H_4$, and 2,6-pyridyl.

A close look at a molecular model reveals that the two α-dioxime groups within one ligand unit are not parallel to each other, which renders a binuclear structure with a ligand to iron molar ratio of 1 : 1 impossible.

The properties and structure of these chelates are compared with those of the monomeric iron(II)-α-dioximes.

Experimental

Preparation of the tetraoxime ligands. 4,4′-Bis(α,β-dioxopropyl)diphenyl-tetraoxime and 4,4′-bis(α,β-dioxopropyl)diphenylether-(1,1)-tetraoxime were prepared according to the methods described by Jones *et al.*[3] The products obtained showed the following characterstics:

4,4′-Bis(α,β-dioxopropyl)diphenyl-tetraoxime. White crystals; soluble in DMSO, hot DMF and hot pyridine; insoluble in methanol, ethanol, ethyl ether, petroleum ether, *etc.*; mp 358—359°C.

Found: C, 61.41; H, 5.07; N, 15.67%.

4,4′-Bis(α,β-dioxopropyl)diphenylether-(1,1)-tetraoxime. White crystals; soluble in DMSO, hot DMF and hot pyridine; insoluble in methanol, ethanol, ethyl ether, petroleum ether, *etc.*; mp 270—271°C.

Found: C, 58.28; H, 4.98; N, 15.22%.

2,6-Bis(α,β-dioxopropyl)pyridine-tetraoxime. The pyridine ligand was newly prepared according to the following method.

Pyridine-2,6-dicarboxylic acid chloride. This compound was obtained by heating a mixture of 25 g (0.15 mol) pyridine-2,6-dicarboxylic acid and 53.5 g (0.45 mol) of freshly distilled thionylchloride on a water bath for 1 hr. The excess thionylchloride was removed by azeotropic distillation with benzene. The product was not further purified, and immediately dissolved in 50 m*l* dry benzene for the next step.

N,N,N′,N′-*Tetraethylpyridine-(2,6)-diamide.* The compound was synthesized by the Schotten-baumann reaction in dry benzene using 51.2 g (0.7 mol) freshly distilled benzene to yield colorless crystals, soluble in all common solvents, yield 78%, mp 73—75°C.

Found: C, 65.25; H, 8.65; N, 15.30%. Calcd for $C_{15}H_{23}N_3O_2$: C, 65.95; H, 8.35; N, 15.15%.

2,6-Dipropionylpyridine. This compound was obtained by the reaction of *N,N,N′,N′*-tetraethyl-pyridine-(2,6)-diamide with ethylmagnesium bromide in anhydrous ether. Due to the low solubility of the diamide in ether, the Grignard reagent was added slowly to a suspension of the former in the solvent. The compound, after extraction with a benzene-ether mixture (1 : 1), was purified by consecutive column chromatography to yield colorless crystals, soluble in all common organic solvents, yield 33%, mp 64—65°C.

Found: C, 68.94; H, 6.86; N, 7.32%. Calcd for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33%.

2,6-Bis(α,β-dioxopropyl)pyridine-2,2′-dioxime. The dioxime compound was obtained from 2.1 g (0.011 mol) of 2,6-dipropionyl-pyridine and 2.2 g (0.022 mol) freshly distilled *n*-butylnitrite in anhydrous benzene, dry hydrogen chloride being bubbled through the reaction mixture. The precipitate was filtered and thoroughly washed with water and benzene. Recrystallization from aqueous alcohol yields colorless crystals, yield 69%, mp 212—213°C.

Found: C, 52.70; H, 4.56; N, 16.80%. Calcd for $C_{11}H_{11}O_4N_3$: C, 52.99; H, 4,45; N, 16.85%.

2,6-Bis(α,β-dioxopropyl)pyridine-tetraoxime. An aqueous-methanolic solution of 1.5 g (0.006 mol) dioxime and 0.84 g (0.012 mol) hydroxylamine-hydrochloride was refluxed for 13 hr, until no more precipitation took place. The precipitate was collected, filtered, washed with cold methanol and dried in a vacuum. Recrystallization from aqueous alcohol yielded colorless crystals, soluble in hot alcohol,

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[1] Presented at the Annual Meeting of the Chemical Society of Japan, April, 1971.

[2] R. J. Cotter and M. Matzner, "Ring-forming Polymerizations," Academic Press, New York and London, (1969), and references therein.

[3] M. E. B. Jones, D. A. Thornton, and R. F. Webb, *Makromol. Chem.*, **49**, 62 (1961).

[4] Sh. Murahashi and H. Kubota, This Bulletin, **35**, 1465 (1962).

TABLE 1. ANALYSES AND MAGNETIC MOMENTS OF THE IRON(II)-COMPLEXES WITH TETRAOXIMES, CH_3-C(NOH)-C(NOH)-R-C(NOH)-C(NOH)-CH_3[a)]

	Found, %			Calcd, %			μ_{eff}, B.M.[b)]
	C	H	N	C	H	N	
(C_6H_4-O-C_6H_4)TOH_2·Fe	49.34	4.68	12.84	50.96	3.80	13.20	2.49
(C_6H_4-C_6H_4)TOH_2·Fe	53.47	5.14	13.84	52.96	3.95	13.72	2.00
(2,6-pyridyl)TOH_2·Fe	39.43	3.88	21.80	39.66	3.32	21.02	2.31

a) Tetraoximes with various R are abbreviated as R-TOH_4.
b) Obtained for the powdered sample at room temperature.

DMSO, DMF, and pyridine, yield 56%, mp 241—242°C. Found: C, 47.19; H, 5.15; N, 24.43%. Calcd for $C_{11}H_{13}O_4N_5$: C, 47.31; H, 4.69; N, 25.08%.

Preparation of the complexes. One millimole of an iron(II) salt (Mohr's salt) was dissolved under nitrogen in 5 m*l* of water; to this solution was added at 50°C a solution of 0.5 mmol tetraoxime ligand dissolved in 10 m*l* hot DMF and 3 m*l* pyridine. An intensely red colored precipitate was immediately formed. The reaction mixture was kept at 50°C until the precipitation was completed (about 8 hr). The product was then filtered, washed with hot water, hot DMF and dried. The red powders obtained were insoluble in all common solvents, except pyridine and other organic bases. They were slightly soluble but unstable in DMF and DMSO. The analytical data are shown in Table 1.

Preparation carried out in pyridine yielded products identical to those obtained by the above standard procedure.

Apparatus and Procedures. Infrared spectra were measured by the KBr disk method using a Shimadzu IR-27C spectrophotometer in the 4000—650 cm^{-1} region. The polystyrene spectrum was used for calibration.

Magnetic moments in the solid state were determined by the Gouy method using freshly distilled water and $CuSO_4 \cdot 5H_2O$ as reference substances. The molar susceptibilities were corrected using Pascal's constants for the diamagnetism of the component atoms.

Reflectance spectra of the finely ground samples were obtained with a Hitachi Spectrophotometer EPS-3, equipped with a reflectance attachment. Magnesium oxide was used as the standard of light reflectance. Electronic absorption spectra were determined with the same spectrophotometer.

The thermogravimetric analyses (TGA) were carried out using a Rigakudenki automatic recording thermobalance under atmospheric pressure. A sample of about 80 mg was held in a nitrogen stream and heated at a rate of 5°C/min.

ESR spectra were measured in the solid state at room temperature and in pyridine solution at room temperature as well as at the temperature of liquid nitrogen with a Japan Electron Optics Laboratory ESR spectrometer, Model JES-ME-2X, using 100 kHz field modulation. A blank test was run before each measurement using an evacuated sample tube. The magnetic field was calibrated with the EPR marker manganese(II) in magnesium(II) oxide.

Results and Discussion

The analytical data of the complexes, shown in Table 1, are in fair agreement with those calculated for a ligand to iron ratio of 1 : 1, indicating that one mole of ferrous ion coordinates with two α-dioxime groups.

The thermogravimetric curves of the metal chelates (*cf.* Fig. 1) show that a thermal decomposition takes place according to the same pattern as for the three complexes. They give further evidence that no axial base is actually coordinated.[5)]

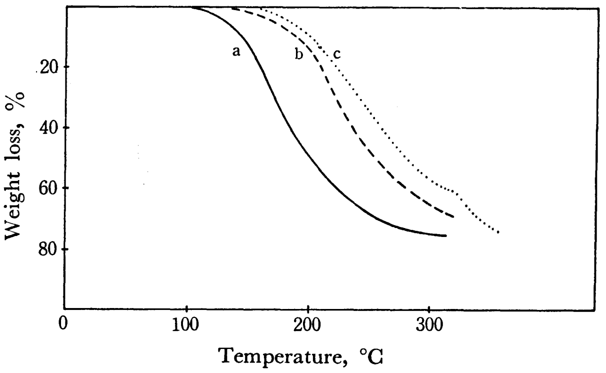

Fig. 1. Thermogravimetric curves of the iron(II)-tetraoximes in nitrogen atmosphere.
a : (C_6H_4-O-C_6H_4)TOH_2·Fe
b : (C_6H_4-C_6H_4)TOH_2·Fe
c : (2,6-pyridyl)TOH_2·Fe

The present ferrous tetraoxime complexes are soluble in organic bases such as pyridine, aniline, *etc.* The electronic absorption spectra in pyridine solution show two intense bands at about 18 and 25 kK. This spectral feature is also found in pyridine-substituted iron(II)-dimethylglyoxime complexes, where two absorption maxima appear in the 17.5—19.6 and the 25.0—25.6 kK regions. The one at longer wavelength is attributed to the Fe→oxime charge transfer, the one at shorter wavelength to the Fe→pyridine charge transfer.[6)]

Though the three polymer chelates have all been found to be paramagnetic in the solid state (*cf.* Table 1), the above absorption pattern is consistent with a diamagnetic species.[6)] Spin-pairing is thus thought to take place upon substituting an axial base.

Support for this conversion was found in the ESR spectra of the compounds. For the solid state samples a clear signal without hyperfine structure was detected in the 3000 Gauss region. This signal completely disappeared in a pyridine solution.

Upon dissolving the chelates in organic bases such as piperidine or aniline which do not allow any axial

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[5)] The TGA curve of ferrous tetraoxime compounds with axially coordinated pyridine, $(CH_2)_nTOH_2$-Fe-$(Py)_2$, $n=6$, 10, shows a weight loss corresponding to the dissociation of two pyridine molecules.

[6)] M. J. Cowan, J. M. F. Drake, and R. J. P. Williams, *Discuss. Faraday Soc.*, **27**, 217 (1959), and references therein; Y. Yamano, I. Masuda, and K. Shinra, This Bulletin, **44**, 1581 (1971).

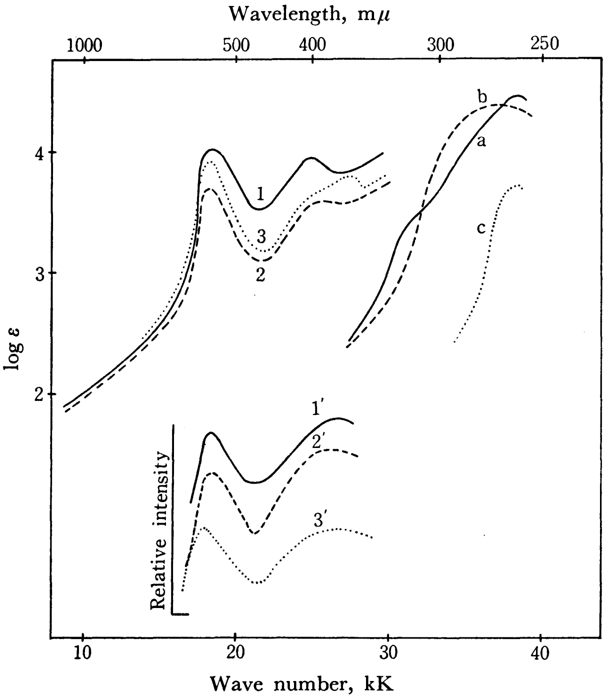

Fig. 2. Absorption spectra: a: $(C_6H_4\text{-O-}C_6H_4)TOH_4$, b: $(C_6H_4\text{-}C_6H_4)TOH_4$, c: (2,6-pyridyl)$TOH_4$, in dimethylsulfoxide solution; 1: $(C_6H_4\text{-O-}C_6H_4)TOH_2\cdot Fe$, 2: $(C_6H_4\text{-}C_6H_4)TOH_2\cdot Fe$, 3: (2,6-pyridyl)$TOH_2\cdot Fe$, in pyridine solution.
Reflectance spectra: 1′: $(C_6H_4\text{-O-}C_6H_4)TOH_2\cdot Fe$,
2′: $(C_6H_4\text{-}C_6H_4)TOH_2\cdot Fe$, 3′: (2,6-pyridyl)$TOH_2\cdot Fe$.

π-delocalization, the absorption band at higher energy, as for the dimethylglyoxime complexes, is no longer found. The band at lower energy, attributed to the Fe→oxime charge transfer, shifts considerably to longer wavelength with the increase of the basicity of the axial substituent (*cf.* Table 2).

In the case of the ferrous dimethylglyoxime complexes, substitution on the axially coordinated pyridine ligand was found to cause strong shifts of the charge transfer bands to longer or to shorter wavelength, depending on whether the donor properties (*cf.* aminopyridine, methylpyridine) or the acceptor properties (*cf.* cyanopyridine) of the pyridine were increased.[6] As can be seen from Table 2, this effect is considerably weaker in the tetraoxime complexes.

A plot of the absorption intensity of the complexes *vs.* the composition of a mixed pyridine-chloroform solvent (Fig. 4) indicates that the axial pyridine forms a very weak bond, which is consistent with the small effect of the pyridine substituents.

It is worth noticing that both the lower and the higher energy bands are shifted to longer wavelength in the pyridine-substituted tetraoxime complexes

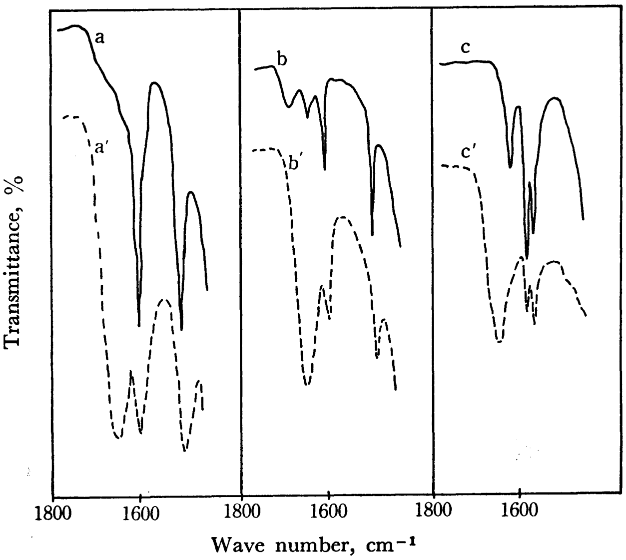

Fig. 3. Infrared spectra of the tetraoxime ligands and their iron(II)-complexes.
a: $(C_6H_4\text{-O-}C_6H_4)TOH_4$, b: $(C_6H_4\text{-}C_6H_4)TOH_4$,
c: (2,6-pyridyl)TOH_4, a′: $(C_6H_4\text{-O-}C_6H_4)TOH_2\cdot Fe$,
b′: $(C_6H_4\text{-}C_6H_4)TOH_2\cdot Fe$, c′: (2,6-pyridyl)$TOH_2\cdot Fe$.

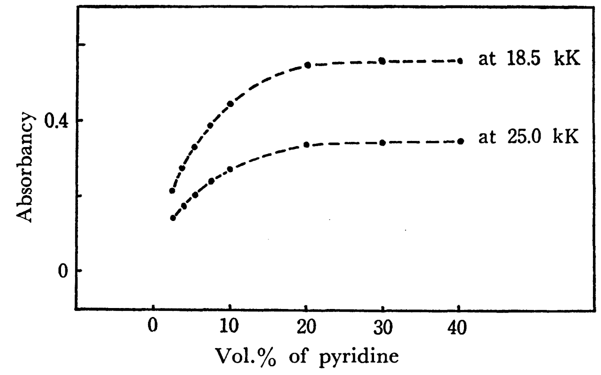

Fig. 4. Absorbancy *vs.* concentration of pyridine.
1.4 mmol $(C_6H_4\text{-O-}C_6H_4)TOH_2\cdot Fe$ in pyridine/chloroform solution, cell length = 1 cm.

Table 2. Electronic absorption spectra

Complexes	ν_{max}, kK (log ε)		Solvents
$(C_6H_4\text{-O-}C_6H_4)TOH_2\cdot Fe$	18.4	26.2	20% (4-CN-Py)/$CHCl_3$
	18.5 (4.11)	25.0 (3.87)	Pyridine
	18.5	25.0	20% (3-CH_3-Py)/$CHCl_3$
	18.4	25.8	20% (3-NH_2-Py)/$CHCl_3$
	18.2		Aniline
	17.3		Piperidine
$(C_6H_4\text{-}C_6H_4)TOH_2\cdot Fe$	18.3 (3.70)	25.6 (3.58)	Pyridine
(2,6-pyridyl)$TOH_2\cdot Fe$	18.4 (3.92)	24.8 (shoulder)	Pyridine
		27.5 (3.79)	

(25.0 and 18.5 kK respectively), as compared to the pyridine-substituted dimethylglyoxime complexes (26.0 and 19.6 kK), which can be related to a stronger Fe→oxime bonding in the former.

Comparision of the infrared spectra of the ligands and the iron(II)-complexes reveals a divergent behavior from similar dimethylglyoxime compounds. Figure 3 shows that the complexing of the nitrogen atoms of the oxime compound leads to the appearence of a strong absorption band at about 1650 cm^{-1}.

For the diphenylether- and the diphenyl-tetraoxime ligands, an absorption band attributable to the C=N stretching vibration can hardly be assigned due to the low intensity absorptions in the characteristic 1650 cm^{-1} region. In the pyridine tetraoxime ligand, a sharp but low intensity band appears at 1620 cm^{-1}, which is tentatively assigned to the C=N stretching mode of the free oxime group. For the three complexes, coordination with Fe(II) leads to a strong, broad absorption band at about 1650 cm^{-1}. A similar effect has been found in 1,2-diimine compounds upon chelating with iron(II).7)

A second noticeable feature of the infrared spectra is that in both the pure ligands and the complexes the OH stretching vibrations at 3250 cm^{-1} can be detected, which in the iron complexes can be assigned to terminal oxime groups within the polymer. The strong intensity of this absorption band within the complexes suggests that the polymer chain is not much extended.

The structure of the ferrous tetraoxime polymer chelates in solvents involving organic bases has so far been found to bear a close resemblance to the axially substituted, octahedral Fe(II)-dimethylglyoxime analogues. While the latter are very unstable in the absence of an axial base,6) the former could be isolated in the solid state, even from a pyridine solution with no pyridine coordinated.

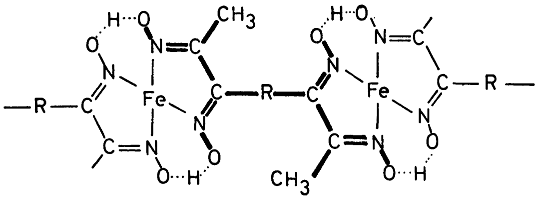

Fig. 5. Schematic representation of the tetraoxime-iron(II) complexes.

However, the reflectance spectra show the presence of a band in the 25 kK region, along with the Fe→ oxime charge transfer band at about 18 kK.

It is clear from a molecular model that, due to the sp^2 bonding between R and the oxime group, the R–C–C angle is equivalent to 120°, which excludes the formation of a monomeric binuclear complex (Fig. 5).

The absorption at shorter wavelength seems to result from an axial interaction of the central ferrous ion with another chelate molecule in the upper and lower-layers of the polymer network forming a pseudo-octahedral structure in the solid state.

Insufficient solubility and infusibility did not allow any accurate molecular weight determination.

Some paramagnetic ferrous chelates with small magnetic moments have been reported.8) Among the explanations offered were impurities from residual ferrous or ferric ions, a thermal mixture of the low spin and the high spin form9) or a planar arrangement with a large ligand field splitting.10)

The present polymer chelates have been found to form a strong bonding in the $Fe–N_4$ plane, whereas the bonding toward the axial substituents is very weak. This seems to be a major factor determining the small magnetic moment.

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10) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1961**, 285.