*An Attempt to Prepare Linear Chelate Polymers**

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Three new tetraoximes, in which two pairs of glyoxime groups are linked together by hexamethylene, decamethylene or a *p*-phenylene group, have been synthesized. The possible formation of coordinated high polymers by the coordination reaction between these tetraoximes and some metal ions has been studied. In the case of aliphatic tetraoximes, instead of the expected coordinated linear polymers, cyclization was found to have occurred, giving multi-membered ring compounds of a low molecular weight. The aromatic tetraoxime also gave coordination compounds, but the product was infusible and insoluble in all solvents tested. Although there was a possibility of obtaining high polymers and the possibility may be considered reasonable from the study of molecular models, the high polymeric nature of the product could not be fully established experimentally.

The main chain of synthetic high polymers is usually linked by covalent bonds. Recently there have appeared in the literature descriptions of some polymeric materials having coordinated bonds with metal ions in the main chain. Such polymeric materials would be of interest from the standpoint of practical importance as well as of academic interest, since they lie on a borderline between organic and inorganic polymers and could be expected to introduce an inorganic character into conventional organic polymers.

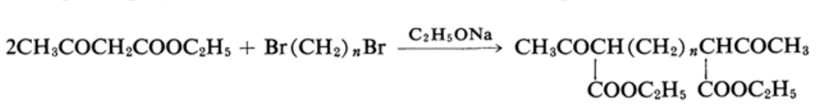
Owing to their insolubility in general, there had been no reliable proof of the formation of high polymers before the present authors started their work. The reaction between dimethylglyoxime and the nickel ion has been well studied in chelate chemistry, and the structure of the complex of nickel(II) dimethylglyoximate has been established as having stable coordination bonds in it.

Attempts were made, therefore, on the basis of the above considerations, to prepare linear coordination polymers which would have stable coordination bonds in the main chain and would be easily soluble in organic solvents.

Three new tetraoximes with two symmetrically situated glyoxime groups were synthesized. One has two glyoxime groups connected by a *p*-phenylene group, which will give little flexibility to the main chain of the resulting polymer owing to the rigidity of the *p*-phenylene group. The other two have their oxime groups connected with polymethylene groups of a different number, which will dilute the mutual polar effect of the glyoxime groups and give more or less flexibility. The reaction between these oximes and metal ions, especially the nickel ion, was carried out.

Results

Bis-α-dioximes were synthesized in the following scheme:



$$2CH_3COCH_2COOC_2H_5 + Br(CH_2)_nBr \xrightarrow{C_2H_5ONa} CH_3CO\underset{COOC_2H_5}{\underset{|}{CH}}(CH_2)_n\underset{COOC_2H_5}{\underset{|}{C}}HCOCH_3$$

$$\xrightarrow[(2)\ NaNO_2,\ H_2SO_4]{(1)\ NaOH} CH_3COC(:NOH)(CH_2)_nC(:NOH)COCH_3$$

(I) $n=6$
(II) $n=10$

$$\xrightarrow{NH_2OH} CH_3C(:NOH)C(:NOH)(CH_2)_nC(:NOH)C(:NOH)CH_3$$

(IV) $n=6$
(V) $n=10$

$$ClCOC_6H_4COCl \xrightarrow{(C_2H_5)_2NH} (C_2H_5)_2NCOC_6H_4CON(C_2H_5)_2$$

$$\xrightarrow{C_2H_5MgBr} CH_3CH_2COC_6H_4COCH_2CH_3 \xrightarrow[CH_3ONO,\ HCl]{} CH_3C(:NOH)COC_6H_4COC(:NOH)CH_3$$

$$\xrightarrow{NH_2OH} CH_3C(:NOH)C(:NOH)C_6H_4C(:NOH)C(:NOH)CH_3$$

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* Presented at the meeting of the Society of Polymer Science, Tokyo, June, 1957.

The intermediate I, II and III hydroxyiminoketones as well as the IV, V and VI tetraoximes are all new compounds; their infrared spectra are presented in Figs. 1 and 2. The I, II and III compounds have absorption bands for the carbonyl and hydroxy groups at 1640～1680 and at 3200～3400 cm^{-1} respectively. In IV, V and VI, the strong absorption band of the carbonyl group disappeared, and instead a strong and broad band for hydroxyl group was seen at around 3250 cm^{-1}. Many geometrical isomers of each one of the tetraoximes may exist; attempts were made to determine whether the product was a mixture of isomers or not, but only one species, presumably the most stable one, was isolated.

Coordination compounds of tetraoximes with metal ions have been prepared by the reaction of tetraoximes with metal salt in dry dimethylformamide or in an aqueous dimethylformamide solution in the presence of or absence of ammonia. The properties of the coordination compounds are shown in Table I. The oximes were allowed to react with Cu^{2+}, Co^{2+} and Fe^{2+} to yield precipitates of black, dark brown, and brown color respectively, but the reaction medium did not show any appreciable increase in viscosity during the reaction. The coordination compounds with nickel ion were all microscopically amorphous, but the VII and IX complexes showed crystalline X-ray patterns (Figs. 3 and 4).

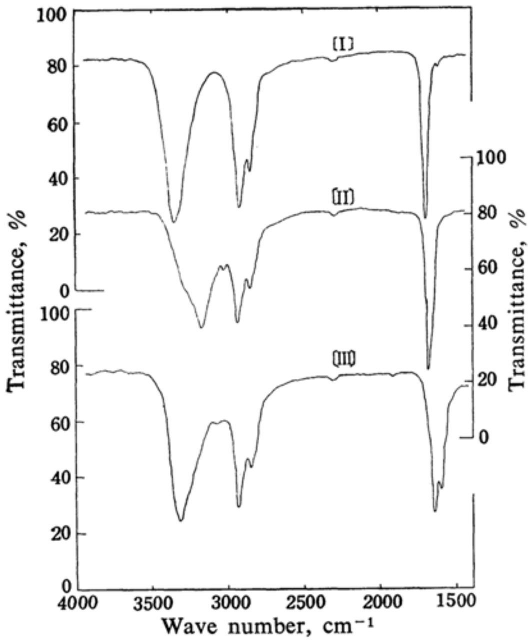


Fig. 1. Infrared spectra of hydroxyiminoketones [I], [II] and [III].

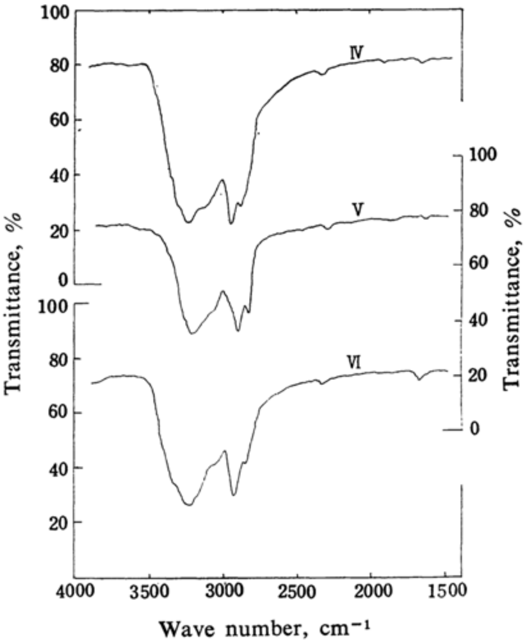
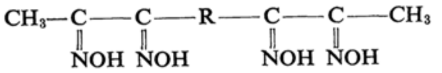


Fig. 2. Infrared spectra of tetraoximes [IV], [V] and [VI].

TABLE I. Ni-CHELATE COMPOUNDS OF THE TETRAOXIMES

Tetraoxime		Ni-Chelate compound				
	R in oxime*		Appearance	Mol. wt. found.	Solvent	Towards aq. alkali hydroxide
IV	$-(CH_2)_6-$	VII	Orange-red powder	400～600	Sparingly sol. in hot pyridine	Stable
V	$-(CH_2)_{10}-$	VIII	Orange-yellow powder	560～620	Pyridine, hot nitrobenzene. Sparingly sol. in chloroform and hot benzene	Stable
VI	$-C_6H_4-$	IX	Orange-red powder	—	None	Became dark red

* General formula



$$CH_3-\underset{\|}{\overset{}{C}}-C-R-C-C-CH_3 \quad \text{with each C} = NOH$$

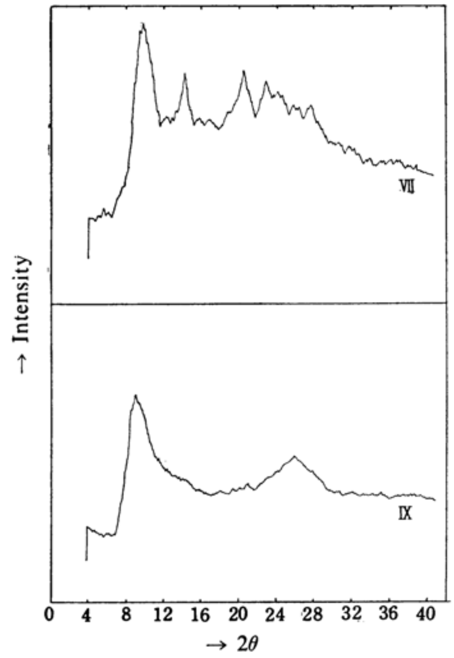


Fig. 3. X-Ray powder spectra (Cu K_α) of [VII] and [IX].

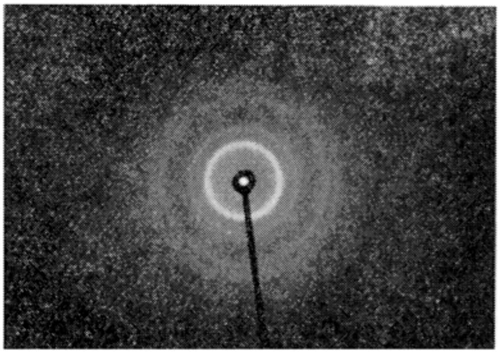


Fig. 4. X-Ray diffraction pattern of (VII). (CuK_α).

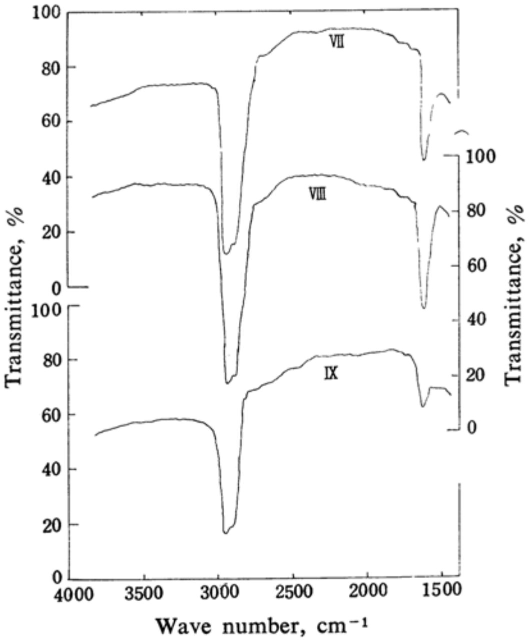


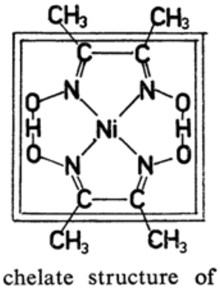
Fig. 5 Infrared spectra of Ni-complexes [VII], [VIII] and [IX].

The infrared spectra of these coordination compounds are shown in Fig. 5. The broad absorption band of tetraoximes at 3250 cm^{-1} disappeared completely, and new bands appeared at 1560 cm^{-1} in VII and VIII and at 1545 cm^{-1} in IX. There are no indications of the presence of the oxime end-group, and the spectra showed a great resemblance to that of nickel(II) dimethylglyoximate. Therefore, it may be concluded that the complete coordination of the glyoxime group to the nickel ion took place. A broad and weak band at about 1775 cm^{-1} in the spectra of VII and VIII, and a very weak one in that of IX, may be considered due to hydrogen bonding in the planar coordination structure around the central nickel ion[1]. It may also be deduced that the glyoxime groups coordinated to the nickel ion have the same structure as that of nickel(II) dimethylglyoximate.

Molecular weight measurement by the Rast method, using *p*-phenylphenol or *p*-nitrophenol as the solvent, showed that VII has a molecular weight of about 400 to 610 (empirical formula weight 343) and VIII, of about 560 to 620 (empirical formula weight 399). The molecular weight of IX was not measured because of its insolubility in the solvents.

Discussion

The coordination structure of nickel(II) dimethylglyoximate is known to be planer with the central nickel ion and with the two hydrogen bonds between the two dimethylglyoxime molecules, as is shown below[2].



The planer chelate structure of nickel(II) dimethylglyoximate

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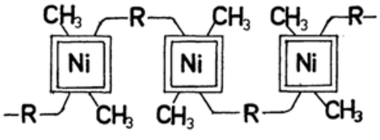
1) R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

2) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

The planer units are piled up on one another in the crystal. On the basis of the above-mentioned facts, the coordination complexes of the tetraoximes with the nickel ion are considered to have the same chelated structure as that of nickel(II) dimethylglyoximate. Leaving aside the problem of steric effect and the tendency of ring formation, and the possible structures of complexes can be represented as either one or as a mixture of the A, B, C and D forms.

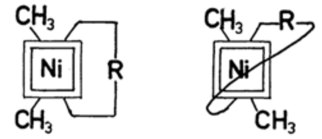
According to the inspection of the Stuart model, the A structure is possible for all the tetraoxime complexes. The B structure is possible only for V, since VII can not take the B structure because of the rigidity of the *p*-phenylene group, nor can IV owing to the shortness of the polymethylene chain. The C structure is probable for IV and V, but is unprobable for VI because of the rigidity of the *p*-phenylene group.

A



Linear polymer

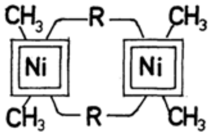
B



cis trans

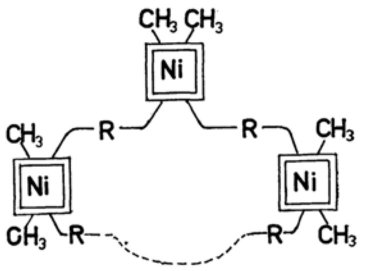
Monomer

C



Dimer

D



Cyclic polymer

Ni = The planer chelate structure with a central nickel atom

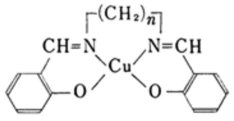
R = -$(CH_2)_6$- IV

R = -$(CH_2)_{10}$- V

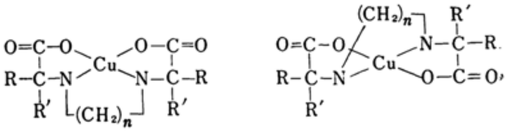
R = -- VI

Except for the A structure with end groups, the forms B, C and D have the same composition and can not be distinguished from each other by mere chemical analysis. In order to draw a conclusion about the structural assignment, further information must be acquired from a detailed examination of the product or from measurements of molecular weight.

The formation of cyclic low-molecular-weight compounds by condensation polymerization is known to occur in the case of polyamides and polyesters: it depends on the length of the chain unit and is modified by the existence of aromatic rings. Since Carothers and his co-workers explored this problem, a large amount of evidence has been accumulated indicating that, unless the formation of stable 5- or 6-member rings were expected in the reaction, the linear polymerization could occur exclusively. In chelate chemistry, although it is known that the formation of the 5- or 6-membered chelate ring is most feasible, the formation of larger membered rings are, surprisingly, just as feasible. For instance, Pfeiffer and his co-workers were able without difficulty to prepare 7-, 8- and 13-membered compounds X (n=4, 5 and 10 respectively) by the reaction of the cupric ion with bis-salicylaldehyde-polymethylene diimine[3]. The formation of the XI and XII complexs are other examples described by Schlesinger[4] and Pfeiffer[5] respectively. From these facts, it is apparent that

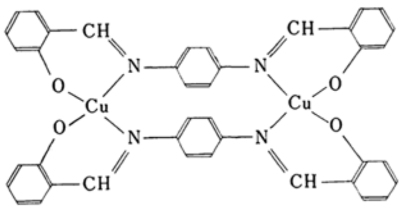


[X] (Pfeiffer)



cis trans

[XI] (Schlesinger)



[XII] (Pfeiffer)

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[3] P. Pfeiffer et al., *Ann.*, **503**, 804 (1933).

[4] N. Schlesinger, *Ber.*, **58**, 1877 (1925).

[5] P. Pfeiffer and H. Pitzer, *J. prakt. Chem.*, **145**, 243 (1936).

the relation between the ring formation and the structural unit in the usual linear condensation polymerisation does not hold in the formation of the co-ordination polymer. Therefore, in assigning the reaction product it seems necessary to study carefully what kinds of unit structure have been or will be favorable to form the linear polymer in each type of coordination compound.

The results of molecular weight measurement indicate that the coordination product VII may be either B or C. The infrared spectrum of VII did not show the absorption band for the oxime end-group, pointing to either a B or C structure, or a mixture thereof. From the study of molecular models, however, the VII compound is considered unable to take the monomeric form B because of the short polymethylene chain. Thus, the VII product may be assigned to the dimer C.

The VIII product also did not show the infrared absorption band for the oxime end-group, and so it may have the structure of either the monomeric B or of the C or D. From the determination of the molecular weight, it may considered to be a mixture of types B and C.

The product IX did not show the oxime end-group in the infrared spectrum and showed a little amorphous character in an X-ray diffraction pattern. From the consideration of molecular models, it may be plausible to consider either the IX product has the A (high molecular weight) or D polymeric structure. However, the polymeric nature of the IX product could not be established definitely owing to its insolubility and infusibility.

Experimental

Dodecane-2, 3, 10, 11-tetraone-3, 10-dioxime (I).— Into a solution of 4.6 g. (0.2 atom) of sodium in 60 ml. absolute alcohol was stirred 30 g. (0.23 mol.) of ethyl acetoacetate. Hexamethylene bromide (27 g., 0.11 mol.) was then added slowly for about one hour at about 100°C (bath temperature). The reaction temperature was maintained at about 100°C until the solution became neutral, about 12 to 15 hr. of continuous stirring being required. Ethanol was distilled off from the reaction mixture by heating it up to 140°C, and there was obtained a viscous brown oil containing a white precipitate. To the oil was added just enough water to dissolve the precipitates and the mixture was extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulfate. Then the ethereal solution was evaporated and the residue was stripped under 5 mmHg until no distillate was obtained by heating it up to 170°C; about 34 g. of brown viscous syrup was obtained.

To the syrup was added a solution of 12 g. (0.3 mol.) sodium hydroxide in 120 ml. water; hydrolysis was effected at room temperature with constant stirring. The heterogeneous mixture was made into a solution in about twenty hours; a clear orange solution was obtained. To this solution was added 16 g. (0.23 mol.) of sodium nitrite, and it was kept below 5°C. An aqueous solution of 10% sulfuric acid was stirred in order to retain the color of potassium iodide-starch paper at least for fifteen minutes.

Aqueous sodium hydroxide was stirred in until all the solid that had separated by the acidification had dissolved. The alkaline solution was extracted with ether to remove any unreacted materials. The alkaline layer was cooled in an ice-salt bath and acidified by stirring in 2 N sulfuric acid. The solid separated by acidification was extracted with ether, producing an orange-red extract. The ether extract was washed with an aqueous 2 N sodium carbonate solution until the aqueous layer became almost colorless. The ether layer was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a solid product, which was recrystallized from a mixture of 10 ml. of ether and 120 ml. of benzene to give 9.6 g. of crude, faintly yellow crystals. The crude product was further recrystallized, using active charcoal, to yield 7.8 g. of colorless crystals; m. p., 129.5~131°C (corr.). The overall yield was 22.6%.

Found: C, 56.24; H, 7.73; N, 10.88. Calcd. for $C_{12}H_{20}O_4N_2$: C, 56.23; H, 7.85, N, 10.93%.

The compound I was easily soluble in ether, alcohol, dimethylformamide and pyridine, was soluble in hot benzene, was sparingly soluble in cold benzene and was insloube in petroleum benzine and petroleum ether. It was soluble in alkali hydroxide solutions, giving a yellow solution, and also a little soluble in concentrated aqueous ammonia, again yielding a yellow solution.

After being heated in a water bath at about 80°C with a nickel salt in an alcohol solution, compound I showed no reaction, but gave, in the presence of ammonia, red precipitates. It gave carbonyl derivatives of hydroxylamine, *p*-nitrophenylhydrazine and semicarbazide. *p*-Nitrophenylhydrazone was soluble in dimethylformamide, pyridine and hot nitrobenzene and was recrystallized from nitrobenzene to give yellow crystals; m. p., 232~233°C (decomp.) (corr.).

Found: N, 21.08. Calcd. for $C_{24}H_{30}O_6N_8$: N, 21.28%.

Dodecane-2, 3, 10, 11-tetraonetetraoxime (IV).—To a mixture of 2.5 g. of I (0.01 mol.), 2 g. of hydroxylamine hydrochloride (0.03 mol.), 1.5 g. of sodium carbonate (0.015 mol.) and 30 ml. of alcohol water was added bit by bit so as to make the mixture clear. The solution was refluxed for more than ten hours and was kept standing overnight. The white precipitates thus formed were filtered and washed with water till no chloride ion were detected. The precipitates were dissolved in 10 ml. of dimethylformamide, and the solution was filtered. Methanol (40 ml.) was then added to the solution and the mixture was kept at room temperature overnight to yield 2 g. of colorless crystals, which decomposed at 250~253°C (corr.). Yield, 70%.

Found: C, 50.39; H, 7.50; N, 19.21. Calcd. for $C_{12}H_{22}O_4N_4$: C, 50.33; H, 7.74; N, 19.57%.

Compound IV was soluble in almost all organic solvents. It was also soluble in an alkali hydroxide solution.

The reaction of IV with Ni^{2+}, Co^{2+} and Cu^{2+} salts in aqueous dimethylformamide solutions immediately gave orange, dark brown and almost black precipitates respectively in the presence of ammonia or alkali hydroxide. In the absence of an alkali catalyst, the reaction took a long time by standing at room temperature and several hours by heating.

Nickel Complex of Dodecane-2, 3, 10, 11-tetraone-tetraoxime (VII).—Nickel was purified through its hexammine complex. Hexaamminenickel bromide (0.231 g. 0.5 mmol.) was decomposed by boiling it with water until no more evolution of ammonia was detected. A few drops of concentrated hydrochloric acid were added, and the solution was evaporated on a water bath. This procedure was repeated several times, a yellowish-brown residue being obtained. To this residue was added just enough water to dissolve the residue, 2 ml. of dimethylformamide and a few drops of concentrated aqueous ammonia, resulting in a homogeneous solution. A solution of 143 mg. (0.0005 mol.) of IV in 6 ml. of dimethylformamide was added to the solution, an orange precipitates being formed immediately. The mixture was heated on a steam bath for 20 hr. and kept standing overnight. The precipitates were filtered out, washed with hot dimethylformamide to remove the unreacted tetraoxime, with water until no more Ni^{2+} and Cl^- were detected, and finally with methanol, and then dried in vacuo at 100°C to yield 150 mg. (92.6%) of the VII complex of an orange color.

Found: C, 41.90; H, 5.81; N, 16.66; Ni, 17.23. Calcd. for $C_{12}H_{20}O_4Ni$: C, 42.05; H, 5.88; N, 16.34; Ni, 17.11%.

The compound showed neither a definite melting point nor a decomposition point. Upon being heated over 300°C in a capillary tube, it changed to a black powder. It was slightly soluble in hot pyridine to give an orange-red solution, was sparingly soluble in nitrobenzene and was insoluble in a wide variety of organic solvents. It was insoluble in 4 N sodium hydroxide and was decomposed with 6 N sulfuric acid and formic acid, but it was not attacked by boiling acetic acid.

Hexadecane-2, 3, 14, 15-tetraone-3, 14-dioxime (II).—The preparation was carried out in the same way as that of compound I. From 4.6 g. of sodium (0.2 atom.), 100 ml. absolute alcohol, 30 g. of ethyl acetoacetate and 33 g. of decamethylene bromide (0.11 mol.), 40 g. of the condensation product was obtained. Hydrolysis of the condensation product and the following formation of oxime gave a crude product, II, which was recrystallized from a benzene-ether mixture to give colorless crystals; m. p., 138∼139°C (corr.). The overall yield was 5.4 g. (17.2%).

Found: C, 61.63; H, 8.85; N, 8.87. Calcd. for $C_{16}H_{28}O_4N_2$: C, 61.51; H, 9.03; N, 8.97%.

The compound was soluble in alcohol, ether and hot benzene and sparingly soluble in cold benzene, but it was insoluble in petroleum benzine or in petroleum ether. The behavior of this compound was similar to that of I.

Hexadecane-2, 3, 14, 15-tetraone-tetraoxime (V).—Preparation of this compound was carried out in the same way as that of IV. The yield of oximation was 88%; m. p., 240∼242°C (corr.).

Found: C, 56.40; H, 8.70; N, 16.07. Calcd. for $C_{16}H_{30}O_4N_4$: C, 56.12; H, 8.83; N, 16.36%.

Compound V was soluble in dimethylformamide, in pyridine, and in hot nitrobenzene, but insoluble in a wide variety of other organic solvents.

Reactions of V with Ni^{2+}, Co^{2+} and Cu^{2+} salt in an aqueous dimethylformamide solution gave orange, dark brown and black precipitates respectively when heated for several hours, or immediately in the presence of ammonia.

Nickel Complex of Hexadecane-2, 3, 13, 14-tetraone-tetraoxime (VIII).—The preparation was carried out in the same way as that of VII, except that the mixture was kept for a week at room temperature (93.3% yield).

Complex VIII was an orange yellow powder, showing no melting point. When heated, it sintered at about 165°C and changed to a black solid at from 220 to 360°C.

Found: C, 48.60; H, 6.93; N, 14.07; Ni, 14.77. Calcd. for $C_{16}H_{28}O_4N_4Ni$: C, 48.15; H, 7.07; N, 14.04; Ni, 14.71%.

Complex VIII was hydrophobic and soluble in pyridine, yielding an orange-red solution. In hot nitrobenzene it became paste-like at first and, after a long time of heating, dissolved to give an orange-red solution. In chloroform, it became paste-like but was sparingly soluble, forming a faintly yellow solution. It was insoluble in a wide variety of other organic solvents.

It was decomposed with formic acid at room temperature, but it was stable with acetic acid.

Terephthaloyl Chloride.—This compound, obtained by heating the mixture of powdered phosphorus pentachloride and terephthalic acid, recrystallized from ligroin in the form of colorless needles; m. p., 81∼82°C (93% yield).

***N*, *N*, *N'*, *N'*-Tetraethyl Terephthalic Diamide.**—The compound was synthesized from terephthalyl chloride and diethylamine by Schotten-Baumann reaction in benzene. It was recrystallized from benzene in the form of colorless crystals; m. p., 128∼129°C (127°C in the literature[6]) (88.5% yield).

***p*-Dipropionylbenzene.**—The compound was obtained by the method of Maxim from *N*, *N*, *N'*, *N'*-tetraethylterephthalodiamide and ethylmagnesium bromide in ether, with the by-product of 4-propionylbenzodiethylamide. The yield was 56.5% in the form of colorless crystals; m. p., 102.5∼103.5°C (corr.) (100°C in the literature[7]).

Found: C, 75.83; H, 7.42. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.27%.

Dioxime was prepared in the usual manner and was recrystallized from alcohol in the form of colorless crystals; m. p., 226∼228°C (corr.).

Found: C, 65.45; H, 7.28; N, 12.10. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.43: H, 7.32; N, 12.72%.

***p*-Bis(1, 2-dioxopropyl)benzene-2, 2'-dioxime (III).**—*p*-Dipropionylbenzene (5.7 g., 0.03 mol.) was

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[6] N. Maxim, *Ann. Chim.*, [10] **9**, 66.

[7] N. Maxim, *Compt. rend.*, **184**, 690 (1927).

dissolved in 60 ml. of dry benzene, and then dry hydrogen chloride and dry methyl nitrite were introduced to the solution, the temperature being kept below 50°C by constant stirring. The reaction mixture was left standing overnight. The mixture was shaken vigorously after the addition of 60 ml. of water. The precipitates formed were filtered, washed thoroughly with water, dried, and then boiled with 20 ml. of benzene and filtered again. The crude product was recrystallized from aqueous alcohol to give 4.8 g. of colorless needles (64.6% yield).

Found: C, 58.11; H, 4.44; N, 11.06. Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.87; N, 11.29%.

Compound III was soluble in dimethylformamide, tetrahydrofuran, boiling alcohol and boiling ether. It was also soluble in aqueous alkali hydroxide and slightly soluble in aqueous concentrated ammonia, yielding an yellow solution. It did not show any reaction with Ni^{2+} salt in a hot alcohol solution after 8 hr., but, in the presence of ammonia, it formed dark brown precipitates.

***p*-Bis(1, 2-dioxopropyl)benzene-tetraoxime (VI).**—The tetraoxime was prepared by refluxing a mixture of 2.1 g. (0.03 mol.) of hydroxylamine hydrochloride, 1.5 g. (0.015 mol.) of sodium carbonate, and 1.2 g. (0.015 mol.) of *p*-bis(1,2-dioxopropyl)-benzene-2,2′-dioxime in aqueous alcohol for 30 hr. The crude tetraoxime was dissolved in hot dimethylformamide and precipitated by adding methanol, yielding 0.46 g. of colorless crystals, which did not show any melting point (40% yield).

Found: C, 51.77; H, 4.83; N, 19.61. Calcd. for $C_{12}H_{14}O_4N_4$: C, 51.79; H, 5.07; N, 20.14%.

The compound was soluble in hot dimethylformamide and in hot pyridine.

Nickel Complex Compound of *p*-Bis(1, 2-dioxopropyl)benzene-tetraoxime (IX).—The chelate compound of VI with nickel ion was prepared in the same way as that of VII, an orange-red powder being obtained. The unreacted tetraoxime was removed from the product by extraction with hot dimethylformamide. The yield was 83%. Compound IX did not show any melting point or definite decomposition point up to 360°C; it darkened at about 260°C and changed to a black powder at about 300°C.

Found: C, 42.61; H, 3.85; N, 15.96; Ni, 17.72. Calcd. for $C_{12}H_{12}O_4N_4Ni$: C, 43.03; H, 3.61; N, 16.73; Ni, 17.52%.

The compound was insoluble in a wide variety of organic solvents and even in hot phenol, hot nitrophenol and *p*-phenylphenol. It was decomposed by 6 N sulfuric acid and by formic acid at room temperature, but it was not decomposed by boiling acetic acid. It is a marked difference of this complex from the other two that it was slowly attacked by 4 N sodium hydroxide to give a dark red solution.

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