IS-431

vic-DIOXIMES AS ANALYTICAL REAGENTS*

by

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I. INTRODUCTION

The intriguing and exciting story of the vic-dioximes seems to have had its beginning in 1883 with the discovery that benzildioxime existed in more than one form. The struggle that ensued to explain the existence of these isomers developed into one of the most exciting and spirited controversies recorded in the chemical literature. It is unfortunate, indeed, that space limitations will permit the citation of only the most significant contributions to this important part of chemical history.

In 1905 the Russian chemist Tschugaeff[1] observed that the α-dioximes differed from all others in that they reacted with nickel, cobalt, iron, platinum, palladium, and copper salts to form stable compounds which he called dioximines. It was reported that nickel(II) salts reacted with 2,3-butanedionedioxime (dimethylglyoxime) to give a scarlet colored crystalline precipitate which was insoluble in water, slightly soluble in alcohol, ether, benzene, glacial acetic acid, and pyridine. It was also noted that nickel dimethylglyoxime could be sublimed undecomposed. Dimethylglyoxime was soon proposed as a reagent for the qualitative detection of nickel[2] and has since found general

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use for this purpose. The use of dimethylglyoxime for the separation and gravimetric determination of nickel was suggested in 1907 by Brunck[3]. Even though the introduction of this reagent revolutionized the analytical chemistry of nickel, it did not possess all the properties of an ideal precipitant. The solubility of dimethylglyoxime in water has been reported by Christopherson and Sandell[4] to be about 5.47×10^{-3} $\underline{M}$ at 25°. Such a limited solubility, of course, precludes using an aqueous solution of dimethylglyoxime as an analytical reagent. Dimethylglyoxime is commonly used as a 1% solution in alcohol but this has the obvious disadvantage that the excess reagent may very well precipitate when the alcoholic solution is added to an aqueous solution. Many attempts have been made to solubilize dimethylglyoxime with such reagents as sodium hydroxide[5,6], ammonium hydroxide[7,8], sodium peroxide[9,10], and urea[11]. Only the urea method of Banks, Adams, and Richard[11] satisfactorily eliminated the use of an organic solvent and produced a stable aqueous solution, but even this technique only effected an increase in the aqueous solubility of dimethylglyoxime by a factor of 2.76[12]. The obvious need for water-soluble vic-dioximes prompted the development of much improved preparative methods for known reagents as well as the synthesis of entirely new vic-dioximes which might provide the answer to the solubility problem (Table 1).

TABLE I

SOME PROPERTIES OF SEVERAL vic-DIOXIMES

vic-Dioxime[a]	M.W.	M.P., °C.	O-H···O $\lambda_{max.}$, μ	Aq. Sol. at 25° M x 10^3	Aq. Sol. at 25° X_2 x 10^5	Sol. factor[b]	ΔF°, kcal. 25°	ΔH°, kcal. 25°-40°	ΔS°, e.u. 25°
DMG	116	240	3.11	5.5	9.9	2.76	5.46[e]	7.14	5.64
DAG	118	200	2.97	167	-	3.22	-	-	-
N	142	189	2.95	64	115	c	4.01	4.53	1.75
DEG	144	186	3.12	2.8	5.04	7.14	5.87	9.83	13.3
3-MN	156	166	3.02	74	-	4.27	-	-	-
4-MN	156	193	2.94	32	-	4.41	-	-	-
H	156	179	3.05	37.6	67.7	5.66	4.32	7.25	9.82
4-IN	184	184	2.91	6.4	-	6.19	-	-	-
4-TAN	212	202	2.92	0.16	-	15.00	-	-	-
α-F	220	167	-	3.3	-	d	-	-	-

[a] DMG = dimethylglyoxime, DAG = 1,2-diaminoethanedionedioxime (diaminoglyoxime), N = 1,2-cyclohexanedionedioxime (nioxime), DEG = 3,4-hexanedionedioxime (diethylglyoxime), 3-MN = 3-methylnioxime, 4-MN = 4-methylnioxime, H = 1,2-cycloheptanedionedioxime (heptoxime), 4-IN = 4-isopropylnioxime, 4-TAN = 4-tert-amylnioxime, α-F = α-furildioxime.

[b] Solubility factor is ratio of sol. in 50% urea solution to aqueous molar solubility.

[c] Nioxime reacts with urea to form Nioxime·2 Urea·H_2O[11].

[d] α-Furildioxime reacts with urea to form 3,4-bis(2-furyl)-1,2,5-oxadiazole[12].

[e] The standard state for the solute was taken as the hypothetical mole fraction, X_2, of one.

It has long been known that the copper complex of dimethylglyoxime is more soluble in water than the corresponding nickel complex. In fact nickel can be quantitatively separated from copper with dimethylglyoxime[13]. Fleischer[14] recently reported that at 25° the aqueous molar solubility of copper dimethylglyoxime exceeds that of nickel dimethylglyoxime by a factor of 5410. It has also been known for some time that the aqueous molar solubility at 25° of the nickel complex of 2,3-pentanedionedioxime (ethylmethylglyoxime) exceeds that of nickel dimethylglyoxime[15] by a factor of 2.67[16]. The research that has contributed to a better understanding of these solubility relationships will be reviewed.

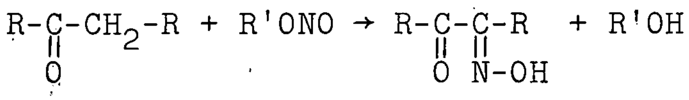
The explanation of why the colors of the various solid nickel(II)-vic-dioxime complexes range from almost purple, through scarlet and orange to yellow eluded the chemist for many years. Even some light has been thrown on this problem in recent years.

II. SYNTHESIS OF THE vic-DIOXIMES

The vic-dioximes have been prepared from a) hydroxyiminoketones, b) vic-diketones, c) brominated ketones, d) epoxydioxindiols, e) cyanogen, and f) dithiooxamide. These preparative schemes will be mentioned briefly but no attempt will be made to discuss them exhaustively.

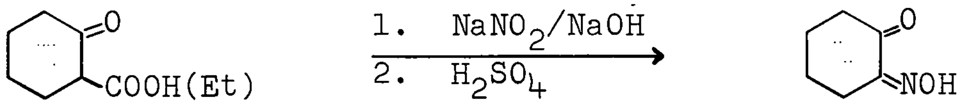
A. From Hydroxyiminoketones

Monoketones with an adjacent methylene group react with alkyl nitrites to form the corresponding hydroxyiminoketone.



$$R\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_2\text{-}R + R'ONO \rightarrow R\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{\|}{N\text{-}OH}}{C}\text{-}R + R'OH$$

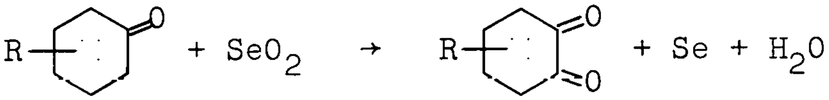
This reaction has been used to prepare diacetylmonoxime[6], 2-hydroxyiminocyclohexanone[17-20], and 2-hydroxyiminocycloheptanone[20]. 2-Hydroxyiminocyclohexanone has also been prepared from either 2-carboxycyclohexanone[21] or 2-ethoxycarbonylcyclohexanone[18,21-26] by treatment with sodium nitrite and sodium hydroxide in a manner first suggested by Takens[27].



Dimethylglyoxime (96%), 1,2-cyclohexanedionedioxime (nioxime) (60%), and 1,2-cycloheptanedionedioxime (heptoxime) (40%) are prepared from the corresponding hydroxyiminoketones by reaction with sodium hydroxylamine monosulfonate in the first case and with hydroxylamine in the latter two cases.

B. From vic-Diketones

The vic-diketones are generally prepared from the corresponding monoketones. Selenium dioxide has been used to oxidize cyclohexanone[18,28-31], many alkylcyclohexanones[32], 4-ethoxycarbonylcyclohexanone[33], and cycloheptanone[34,35].



This reaction allows one to prepare the vic-diketone in yields ranging from 35-90%. The method, however, has the disadvantage of having to handle selenium compounds which can be none too pleasant. 1,2-Cyclohexanedione and 1,2-cycloheptanedione have also been prepared from adipoin[36] and 1,2-bis(ethoxycarbonyl)cycloheptane by hydrolysis[37], respectively. The vic-dioximes in the alicyclic series are easily prepared from the corresponding vic-diketones in yields ranging from 50-80%[30,32,33,35].

The aromatic vic-diketones are almost invariably prepared from the corresponding acyloins. Furil has been prepared from furoin by oxidation with nitrobenzene and sodium ethoxide[38], 90%, or thallous ethoxide[39], 83%; iodine[40], 80%; copper sulfate and pyridine[41], 63%; ammonium nitrate and copper acetate[42,43], 91%; bismuth trioxide[44], 88%; air[45-47], 63%; manganese dioxide[48], 88%; and also by the Oppenauer oxidation with aluminum phenoxide[48-50], 88%. Benzil can be prepared from benzoin by many of the same oxidizing agents as have been used for furil: ammonium nitrate and copper acetate[43], 90%; air[47], 72%; thallous ethoxide[39], 90%; aluminum phenoxide[49,50], 80-87%. Early attempts to prepare α-furildioxime from furil gave very low yields[51,52], but Reed, Banks, and Diehl[53] in 1947 devised a scheme by which this reagent could be prepared in 55% yields. α-Benzildioxime can be prepared from benzil and hydroxylamine[54-56]. The synthesis of the α-vic-dioximes in the aromatic series generally yields some of the β-isomer[56] as well as some of the γ-isomer[57-59].

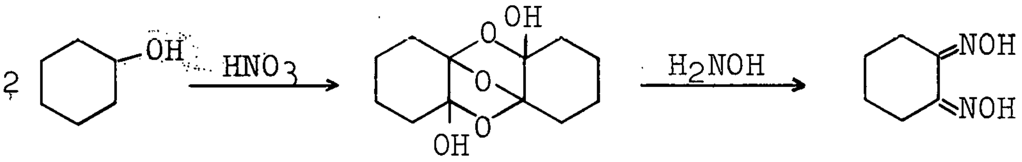
C. From Halogenated Ketones

Hantzsch and Wild[60] in 1896 first pointed out that α-haloketones could be converted to vic-dioximes with hydroxylamine. This reaction has been used by Tokura and Oda[61] to prepare nioxime from 2-chlorocyclohexanone and by Belcher, Hoyle, and West[62] to prepare aliphatic and alicyclic vic-dioximes. The yields of the vic-dioximes are, in general, comparable to previous methods but the method has the disadvantage of involving the often unpleasant experience of working with lachrymatory α-haloketones.

α-Haloketones can also be converted to the corresponding vic-diones[63,64] which in turn may be oximated with hydroxylamine. The Wallach[63] procedure for preparing nioxime gives extremely low yields, but 1,2-cyclohexanedione can be prepared in 43% yield from 2-chlorocyclohexanone by the method of McEntee, et al.[64].

D. From Epoxydioxindiols

Godt and Quinn[65], Godt[66], and also Svoboda and Krátký[67] reported the preparation of octahydro-5aH,10aH-4a,9a-epoxydibenzo-p-dioxin-5a,10a-diol in 50% yield by oxidizing cyclohexanol with nitric acid. This epoxydioxindiol is conveniently oximated with hydroxylamine to give nioxime in yields as high as 90%[67]. This is a most interesting reaction, especially if it can be applied to substituted cyclohexanols and cycloheptanol.



E. By Special Methods

Diaminoethanedionedioxime (oxalamidoxime, oxalenediamidoxime, oxalenediaminodioxime, dicarbamidoglyoxime, oxaldiamidedioxime, oxalenediamidodioxime, niccolox, oxamidedioxime, diaminoglyoxime, oxamidoxime) is easily prepared from hydroxylamine and cynogen[68-71], cyanoaniline[72,73], or dithiooxamide[74,75]. It has also been prepared from dichloroglyoxime and anhydrous ammonia[76].

III. ANALYSIS OF THE vic-DIOXIMES

The vic-dioximes have been determined gravimetrically following precipitation with an excess of nickel[77,78]. This method quite often gives low results. Anderson and Banks[79] have measured the step-wise formation constants for the nickel complexes with various vic-dioximes in water (Table 2) and found that, in general, $k_1 < k_2$. Dyrssen, Krašovec, and Sillén[80] concluded from distribution data that $\log k_1 \leq \log k_2$. From these data it would seem likely that, in the presence of an excess of nickel, appreciable amounts of $NiHD^+$ would be formed and account for the low results mentioned above. Other workers have found that in 50% dioxane, $k_1 > k_2$.[81,82]

TABLE 2

FORMATION CONSTANTS OF NICKEL(II)-vic-DIOXIME COMPLEXES IN WATER[a]

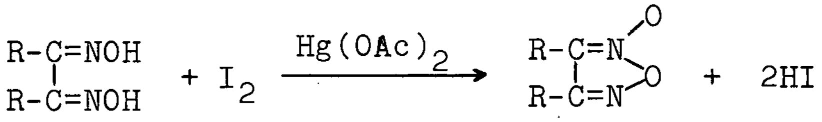
Ligand[b]	$\log k_1$	$\log k_2$
DMG	7.91	9.09
EMG	7.27	9.99
DEG	8.97	8.20
DPG	8.77	8.35
4-IN	8.42	8.34
N	8.52	8.82
3-MN	8.66	9.62
4-MN	8.27	9.71
H	9.63	9.81

[a] Temperature, 25°C.; ionic strength, 0.1.

[b] EMG = 2,3-pentanedionedioxime (ethylmethylglyoxime), DPG = 4,5-octanedionedioxime (dipropylglyoxime).

vic-Dioximes can be hydrolyzed and the resulting hydroxylamine titrated[83,84].

Recently Banks and Richard[85] devised a simple and accurate titrimetric method based on quantitatively dehydrogenating the vic-dioximes in non-aqueous media with iodine and mercuric acetate.



This method gives excellent results with many aliphatic, alicyclic, and aromatic vic-dioximes. The reaction can also be used as a preparative method for furoxanes.

IV. STRUCTURE OF THE vic-DIOXIMES

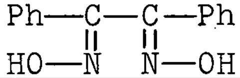
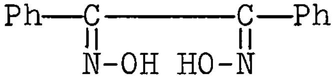
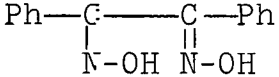
A. Geometrical Isomerism

In 1883 Goldschmidt and Meyer[54] first reported the preparation of α-benzildioxime, m.p. ~240°, and later in the same year Goldschmidt[86] successfully isolated β-benzildioxime, m.p. ~207°. Chemists were not long in accepting the challenge implicit in the polymorphism of benzildioxime. In fact, a serious effort was made to resolve this enigma[87,88] even before Auwers and Meyer[89] prepared the third isomer, γ-benzildioxime, m.p. ~165°. Goldschmidt[90] found that all three isomers reacted with phenyl cyanate and thereby concluded that the isomerism must be stereochemical.

In 1890 Hantzsch and Werner[91] published their classical paper on the stereochemistry of nitrogen and proposed structures for the three known isomers primarily on the basis of their stabilities (Table 3).

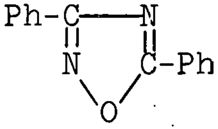
TABLE 3

STRUCTURE ASSIGNMENTS FOR THE THREE BENZILDIOXIMES

	Isomer					
	 $\begin{array}{c}\mathrm{Ph{-}C{-}C{-}Ph}\\ \quad\| \quad \|\\ \mathrm{HO{-}N \quad N{-}OH}\end{array}$		 $\begin{array}{c}\mathrm{Ph{-}C{-}{-}{-}C{-}Ph}\\ \| \qquad \|\\ \mathrm{N{-}OH \; HO{-}N}\end{array}$		 $\begin{array}{c}\mathrm{Ph{-}C{-}{-}C{-}Ph}\\ \| \qquad \|\\ \mathrm{N{-}OH \; N{-}OH}\end{array}$	
Worker(s)	I[a]	Basis	I[a]	Basis	I[a]	Basis
Hantzsch and Werner (91)	β-	Most stable isomer	γ-	Forms anhydride readily	α-	Intermediate properties
Hantzsch (92)	β-	Yields oxanilide[b] by *cis*-Beckmann rearrangement	γ-		α-	Behaves as asymetric compound in *cis*-Beckmann rearrangement
Beckmann and Köster (93)	β-	Yields oxanilide assuming *cis*-Beckmann rearrangement	α-	Yields dibenzenyl-azoxime[c] assuming *cis*-Beckmann rearrangement	γ-	Yields benzoylphenyl carbamide[d] assuming *cis*-Beckmann rearrangement
Meisenheimer (94)	α- *anti*-	Yields dibenzenyl-azoxime by *trans*-Beckmann rearrangement	β- *syn*-	Yields oxanilide by *trans*-Beckmann rearrangement	γ- *amphi*-	Yields benzoylphenyl carbamide by *trans*-Beckmann rearrangement

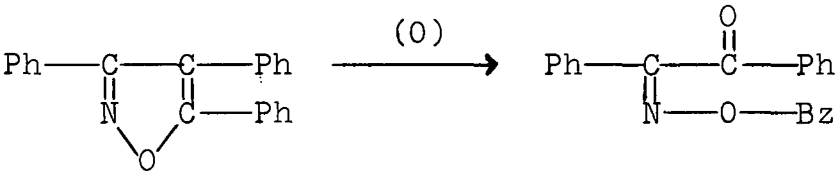
[a] Isomer assigned the configuration appearing above.

[b] PhN(H)C(O)C(O)N(H)Ph

[c] 

[c] PhC(O)N(H)C(O)N(H)Ph

Hantzsch[92] in 1891 and Beckmann and Köster[93] in 1893 assigned structures to the three isomers on the assumption that the Beckmann rearrangement involved the exchange of neighboring or cis-groups. It was not until 1921, however, that Meisenheimer[94] observed that 3,4,5-triphenylisoöxazole upon oxidation with chromic acid or ozone gave a compound which was identical with benzoyl-β-benzilmonoxime and which, by necessity of the manner in which it was formed, must have had the following structure:



This structure was just opposite to that previously assigned to this compound and led Meisenheimer to the conclusion that α- and β-benzilmonoximes must also have configurations opposite to those previously assigned and that the Beckmann rearrangement actually involved the exchange of trans-groups. This discovery, in turn, led to the reassignment of the structures of α-, β-, and γ-benzildioxime (Table 3) to those which are still today considered correct.

It is interesting to note that the different geometrical isomers for the vic-dioximes have only been isolated in the aromatic series. There is little evidence that the β(syn)- or γ(amphi)-isomers exist in either the aliphatic or alicyclic[95] series of vic-dioximes.

B. Oxime-Nitrone Isomerism

Brady and Mehta[96] in 1924 successfully prepared both the O-methylether and the N-methylether of both the <u>syn</u>- and the <u>anti</u>-<u>p</u>-nitrobenzophenoneoxime.

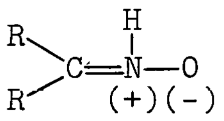
$\begin{array}{c}\mathrm{Ar{-}C{-}Ar'}\\ \|\\ \mathrm{N{-}OCH_3}\end{array}$ $\begin{array}{c}\mathrm{Ar{-}C{-}Ar'}\\ \|\\ \mathrm{CH_3{-}N{\rightarrow}O}\end{array}$

syn-

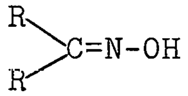
$\begin{array}{c}\mathrm{Ar{-}C{-}Ar'}\\ \|\\ \mathrm{CH_3O{-}N}\end{array}$, $\begin{array}{c}\mathrm{Ar{-}C{-}Ar'}\\ \|\\ \mathrm{O{\leftarrow}N{-}CH_3}\end{array}$

anti-

This evidence strongly suggested that the oximes could exist in a zwitterion structure (nitrone form) as well as the classical (oxime form) structure.



zwitterion



classical

Merritt and Lanterman[97] determined the crystal structure of dimethylglyoxime and found it to be composed of chains of essentially planar, centro-symmetric molecules joined together by a network of hydrogen bonds. This structure determination has recently been further refined by Hamilton[98] in which it was shown that dimethylglyoxime exists in the classical (oxime) rather than the zwitterion (nitrone) form. It was also shown that the O-H···N hydrogen bond angle is ~140° rather than the usually assumed 180°. The crystal structure of dimethylglyoxime is quite consistent with its known high melting point (240°) and its low solubility in water (0.0055 <u>M</u>).

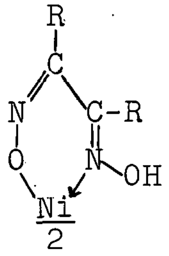
V. STRUCTURE OF THE METAL(II)-vic-DIOXIME COMPLEXES

A. Chemical Evidence

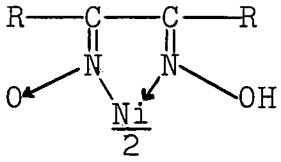
The younger contemporary chemists sometimes fail to fully appreciate the problems that faced the structural chemists at the turn of the century. Even without the availability of the extremely powerful physical tools of today, they made tremendous strides toward understanding the chemistry of the metal(II)-vic-dioxime complexes.

It was known quite early that nickel(II) salts reacted with α-vic-dioximes to form red colored (1:2) precipitates, with the γ-vic-dioximes to give yellow or green-yellow colored (1:1) compounds, and that no reaction was observed with the β-vic-dioximes.

On the basis that the α-vic-dioximes had the amphi-configuration, Werner and Pfeiffer[99] in 1905 proposed a six-membered ring structure for the nickel(II)-α-vic-dioxime complex.



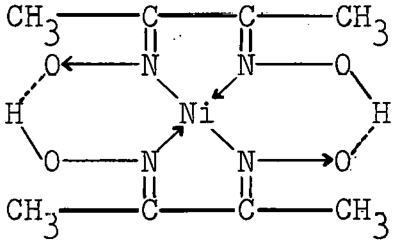
After it was shown that the α-vic-dioximes actually had the anti-configuration, the above six-membered ring structure no longer seemed feasible. On the basis of the evidence presented by Brady and Mehta[96] for the existence of the zwitterion (nitrone) form of the oxime, Pfeiffer and Richarz[100] proposed the following structure.



It was soon shown that the mono-O-ethers of the α-vic-dioximes react with nickel in much the same way as do the α-vic-dioximes[101,102]. In addition, Pfeiffer[101] found that the reaction also occurred if one of the oxime groups was replaced by an imino or methylimino group. These observations indicated that the hydroxy group of the second oxime is not involved in the reaction and that the metal is not linked to the oxygen and gave strong support to the five-membered ring structure.

Nickel dimethylglyoxime does not react with phenyl isocyanate[103] or acetic anhydride[104] and does not react with methyl magnesium iodide in amyl ether to yield methane[102].

It was pointed out by Dubský and Brychta[105] that if symmetrical metal(II)-vic-dioxime complexes such as nickel dimethylglyoxime were planar molecules, the Pfeiffer and Richarz structure could give rise to cis-trans isomers, i.e., both hydroxy groups on same side or on opposite sides of the complex. The unreactivity of the hydroxy group and that no such cis-trans isomerism had ever been observed in the case of nickel dimethylglyoxime, prompted Brady and Muers[102] to propose the following hydrogen bonded structure.



In 1932 Sugden[106] and in 1935 Cavell and Sugden[107] and Dwyer and Mellor[108] prepared the cis- and trans-isomers of the nickel and palladium derivatives of unsymmetrical vic-dioximes, thus proving by chemical means, that these metals form quadricovalent planar complexes with the vic-dioximes. As will be seen, the above molecular structure of nickel dimethylglyoxime, deduced entirely from chemical evidence, agrees remarkably well with the structure currently considered correct.

B. Physical Evidence

Closely following the proposed molecular structure by Brady and Muers[102], it was shown that nickel dimethylglyoxime was diamagnetic[109,110] which, according to Pauling[111], is strong evidence that this quadriligated complex has the square coplanar (dsp^2) structure. More recently, Banks, Vander Haar, and Vander Wal[112] have shown that several other nickel(II)- and palladium(II)-vic-dioxime complexes are also diamagnetic and presumably have the same square coplanar molecular structure as does nickel dimethylglyoxime.

Voter, Banks, Fassel, and Kehres[113] were the first to make a careful infrared spectrophotometric study of the hydroxy group in several nickel(II)-vic-dioxime complexes and the corresponding deuterated complexes. This study showed clearly that the oxime hydrogens of the metal derivatives are present in an O-H-O structure which seemed to be unlike normal hydrogen bonds. Further studies by Godycki, Rundle, Voter, and Banks[114] led them to believe that the O-H-O bond in nickel dimethylglyoxime is unusually strong and perhaps a symmetrical hydrogen bond. Additional work by Rundle and Parasol[115] added credence to the suggestion that these metal complexes contained symmetrical (colinear) hydrogen bonds. Recently, Blinc and Hadži[116] have studied the infrared spectra of various metal(II)-vic-dioxime complexes and have concluded that the O-H-O bonds may very well not be of the symmetrical type and have suggested that they are bifurcated rather than colinear.

Godycki and Rundle[117] were the first workers to provide an accurate crystal structure for nickel dimethylglyoxime. This study definitely proved that crystals of nickel dimethylglyoxime contained square planar molecules stacked one above another, 3.24 Å., apart, so that the nickel atoms lie in a straight row that extends throughout the length of the crystal. Alternate molecules are rotated 90° and packed along c_o in a manner resembling interlocking blocks. Further refinement of this structure determination[118] showed that the O-O distance in the O-H-O hydrogen bond is 2.40 Å., indicating an extremely strong hydrogen bond as did the infrared studies. Godycki and Rundle[117] also proposed that weak nickel-nickel bonding occurs in these crystals and that this type of intermolecular interaction might explain the fact that nickel dimethylglyoxime is less soluble than is copper dimethylglyoxime. Rundle[119] estimated this nickel-nickel bond energy to be about 10 kcal./mole.

It was immediately apparent that if, indeed, nickel-nickel bonding did occur in nickel dimethylglyoxime, it should be possible to prepare substituted vic-dioximes which would offer steric hindrance to the formation of nickel-nickel bonds. Hooker and Banks[120] in 1955 prepared a series of substituted alicyclic *vic*-dioximes to test this thesis. They found that the nickel(II) and palladium(II) complexes of the substituted *vic*-dioximes were, indeed, many times more soluble in chloroform than the corresponding nioxime complexes as predicted. Sharpe and Wakefield[121] estimated the nickel-nickel distance in nickel ethylmethylglyoxime but this measurement was based on the erroneous assumption that the packing in the unit cell was similar for the nickel complexes of dimethylglyoxime and ethylmethylglyoxime. Banks and Barnum[122] carefully measured the metal-metal bond distances in twelve nickel(II) and palladium(II) complexes of the *vic*-dioximes. It was shown that, excepting nickel dimethylglyoxime, the solubility product constants, K_{sp}, increase with increasing metal-metal bond length. Anderson and Banks[79] have determined the intrinsic solubility constant, K_s, and found that it correlated better with the metal-metal bond distance than did the solubility product constant. This was not unexpected because the intrinsic solubility is more closely associated with the crystal energy than is the solubility product constant and might be less subject to ligand effects.

$$\begin{tikzcd}
\mathrm{Ni(HD)_{2(c.)}} \arrow[r, "K_s"] \arrow[dr, "K_{sp}"'] & \mathrm{Ni(HD)_{2(aq.)}} \\
 & \mathrm{Ni^{++}_{(aq.)} + 2HD^{-}_{(aq.)}} \arrow[u, "K_2"']
\end{tikzcd}$$

From Table 4 it is apparent that the intrinsic solubility correlates well with nickel-nickel bond distance for the alicyclic series, however, nickel dimethylglyoxime seems to behave differently. Factors other than metal-metal bond distances must be important.

TABLE 4

SOLUBILITY RELATIONSHIPS AND M-M BOND DISTANCES FOR NICKEL(II)-vic-DIOXIME COMPLEXES

Ligand	pK_{a_1} [a]	log K_2 [a]	pK_{sp}	pK_s	Ni-Ni, Å
DMG	10.48	17.00	23.66	6.66	3.233
EMG	10.51	17.57	23.27	5.70	b
DEG	10.67	17.17	24.21	6.96	b
DPG	10.81	17.12	25.14	8.02	b
4-IN	10.53	16.76	27.84	11.08	3.19
N	10.55	17.34	28.39	11.06	3.237
4-MN	10.54	17.94	28.25	10.32	3.24
3-MN	10.61	18.28	27.62	9.34	3.47
H	10.71	19.44	26.64	7.20	3.596

[a] Temperature, 25°C.; ionic strength, 0.1.

[b] The crystal structures for these complexes are different from that of nickel dimethylglyoxime.

The crystal structure of nickel ethylmethylglyoxime, recently determined by Frasson and Panattoni[123], shows that the presence of nickel-nickel bonds in this complex is not possible but that the O-O distance in the O-H-O bond is only 2.33 Å.

Anderson and Banks[79] have determined the heats of solution for both nickel dimethylglyoxime and nickel ethylmethylglyoxime in a number of solvents in order to estimate the strength of the nickel-nickel bond (Table 5).

TABLE 5

THERMODYNAMIC QUANTITIES[a] FOR THE REACTION: $NiG_{2(c.)} \rightarrow NiG_{2(soln.)}$

	$Ni(DMG)_2$			$Ni(EMG)_2$			
Solvent	ΔF°, kcal.	ΔH°, kcal.	ΔS°, e.u.	ΔF°, kcal.	ΔH°, kcal.	ΔS°, e.u.	$\Delta(\Delta H^\circ)$, kcal.
CCl_4	8.50	15.3	22.8	5.59	4.0	-5.34	-11.3
Heptane	10.15	15.1	16.62	9.19	5.8	-11.39	-9.3
H_2O	10.53	10.25	-0.94	9.96	3.43	-21.9	-6.82
$CHCl_3$	6.06	6.1	+0.15	4.15	2.88	-4.25	-3.2
Benzene	7.05	7.27	+0.73	4.95	7.00	+6.88	-0.27

[a] The standard state for the solute was taken as the hypothetical mole fraction, X_2, of one and 298°K.

It is readily apparent that in non-coordinating solvents such as carbon tetrachloride and _n_-heptane that the crystal energy of the nickel dimethylglyoxime is about 10 kcal. greater than that of nickel ethylmethylglyoxime, and probably is a fairly good measure of the nickel-nickel bond strength.

The crystal structure of copper(II) dimethylglyoxime[124] shows that the crystal is made up of dimers held together by two copper-oxygen bonds 2.43 Å in length and that no copper-copper bonding is possible. Dyrssen and Hennichs[125] have shown that $Cu(HD)_2$ has a much greater tendency to coordinate with water than does $Ni(HD)_2$ and, in fact, may very well dissolve in water to form $Cu(HD)_2 \cdot H_2O$. If when copper dimethylglyoxime dissolves in water, one copper-oxygen bond per copper is broken in the crystal and a similar bond is formed when the hydrate is formed in solution, one would expect the heat of solution for this process to be about zero. Fleischer[126] has observed just this.

It is not surprising that Fleischer also observed that the crystal energy of copper dimethylglyoxime is about equal to or perhaps slightly greater than that of nickel dimethylglyoxime. Apparently the copper-oxygen bonds and the nickel-nickel bonds contribute about equally to the crystal energy of these two crystals. The explaination for the fact that the solubility of copper dimethylglyoxime in water is greater than that for nickel dimethylglyoxime seems to lie in their different tendencies to form hydrates rather than on differences in their crystal energies.

Palladium dimethylglyoxime[127] and platinum dimethylglyoxime[128] have been shown to be isomorphous with nickel dimethylglyoxime.

Yamada and Tsuchida[129] found that for both the nickel(II) and platinum(II) complexes of dimethylglyoxime that maximum absorption of visible light occurs when the electric vector of the polarized light is perpendicular to the plane of the molecules. Banks and Barnum[130] also observed "abnormal" dichroism for a series of nickel(II)- and palladium(II)-_vic_-dioxime complexes and found that this "abnormal" dichroism correlated rather well with the length of the metal-metal bond. This is strong evidence for the presence of metal-metal bonds in these crystals. Copper(II) dimethylglyoxime and nickel(II) ethylmethylglyoxime, neither of which form metal-metal bonds, absorb polarized light most strongly when the electric vector is in the plane of the molecules in a "normal" manner (Table 6).

TABLE 6

DICHROISM OF METAL(II)-*vic*-DIOXIME COMPLEXES

Ligand[a]	-M-M- Bond Distance, Å	Dichroism[b]	References
	Nickel Complexes		
DMG	3.233	abnormal	117,129, 130
N	3.237	abnormal	130
α-B	3.547	abnormal	130
H	3.596	abnormal	130
EMG	c	normal	79,123
	Palladium Complexes		
N	3.250	abnormal	130
DMG	3.253	abnormal	127,130
H	3.329	abnormal	130
	Platinum Complexes		
DMG	3.23	abnormal	128,129
	Copper Complexes		
DMG	c	normal	124,129

[a] α-B = α-benzildioxime

[b] Dichroism is considered to be normal if plane polarized light is more strongly absorbed when $\bar{E}$ is parallel to plane of the molecule.

[c] Crystalline structure determinations show that metal-metal bonding cannot be present.

It now appears that all data are in agreement with the presence of metal-metal bonds in all those complexes having crystal structures like that of nickel dimethylglyoxime and that the strength of this bond in the latter case is about 10 kcal. per mole.

VI. ANALYTICAL APPLICATIONS

The analytical applications of the various vic-dioximes was reviewed in 1940 by Diehl[131]. More recently, Banks et al. have compiled annotated bibliographies on nioxime[132], heptoxime[133], α-furildioxime[134], diaminoglyoxime[135], and α-benzildioxime[136]. Other papers of a review nature have also been published[133,137-143].

A. Gravimetric Methods

Procedures for the gravimetric determination of nickel with dimethylglyoxime[131], nioxime[144-148], nioxime-urea complex[11], heptoxime[146,149-151], 4-methylnioxime[152], 4-isopropylnioxime[152], α-furildioxime[52,153], α-benzildioxime[154-162], and diaminoglyoxime[69,70,163] have been reported. Palladium has been determined by dimethylglyoxime[131], nioxime[164,165], 4-methylnioxime[152], 4-isopropylnioxime[165], α-furildioxime[153,166], and diaminoglyoxime[167]. The procedures of Voter and Banks[146] and of Ferguson, Voter, and Banks[151] for the gravimetric determination of nickel with heptoxime are especially recommended. Banks and Hooker[152] have shown that the 4-alkylnioximes are excellent reagents for the gravimetric determination of palladium as well as nickel.

B. Spectrophotometric Methods

The spectrophotometric methods for the determination of metals with the vic-dioximes are of two types, i.e., those involving heterogeneous media and those involving homogeneous media. Spectrophotometric methods involving an extraction step will be discussed under extraction methods. The heterogeneous spectrophotometric method was first proposed by Armit and Harden[168] in 1905 and was based on measuring the color of an aqueous suspension of nickel dimethylglyoxime. This method has been improved and applied to the determination of nickel in calcium by Ferguson and Banks[169], to the determination of nickel with α-furildioxime[170], and to the determination of cyanide with α-furildioxime[171,172]. The homogeneous spectrophotometric method for nickel is based on the reaction of this metal with a vic-dioxime in an alkaline solution to produce a soluble red color. Dimethylglyoxime was first observed to give this reaction by Feigl[173] in 1924. Rollet[174] in 1925 first used this reaction to determine nickel in steel. In addition to dimethylglyoxime, nioxime[144,169,175], heptoxime[175], and α-benzildioxime[176] have also been used in the Rollet method of determining nickel. The nature of this color reaction has been investigated by many workers but the conclusions reached by these workers have differed substantially. Recently Banks and LaPlante[177] have shown that three complexes are formed between nickel(II) and vic-dioximes in alkaline media, i.e., 1:1, 1:2, and 1:3. In the presence of an oxidizing agent, the nickel(II) appears to be oxidized to nickel(IV) in the 1:3 complex which gradually decomposes to give a nitrooxime. Diaminoglyoxime has been used for the spectrophotometric determination of nickel[178] and of both nickel and cobalt in mixtures of the two[179].

The vic-dioximes react with iron(II) in the presence of amines to give a colored solution which can be used for the spectrophotometric determination of iron[142,180,181]. Banks and

Byrd[182] found that iron(II) reacts with nioxime in acetate buffered solution to form $Fe(HD)_2 \cdot 2H_2O$. In the presence of amines it is probable that the water in the above compound is displaced to give a complex of the type $Fe(HD)_2 \cdot 2RNH_2$.

Rhenium reacts with the α-furildioxime to yield a colored complex which can be used for the spectrophotometric determination of rhenium in aqueous solution[183,184].

C. Extraction Methods

Almost invariably extractions of metal-vic-dioxime complexes into an organic phase merely serves as a preliminary step to a spectrophotometric determination. Nickel has been determined by extracting the heptoxime complex into chloroform[185,186]; the α-furildioxime complex into 1,2-dichlorobenzene[187]; the 4-methylnioxime complex into chloroform[120], and into toluene[188]; the 4-isopropylnioxime complex into chloroform[120], and into xylene[189]. Palladium has been determined by extracting the dimethylglyoxime complex into chloroform[190]; the 4-methylnioxime complex into chloroform[120,191]; the 4-isopropylnioxime complex into chloroform[120]; the α-furildioxime complex into chloroform[192]; and the α-benzildioxime complex into chloroform[193].

The iron(II)-nioxime-pyridine complex can be extracted into benzene and measured spectrophotometrically[194].

Rhenium reacts with dimethylglyoxime[195], α-benzildioxime[196], α-furildioxime[197], and 4-methylnioxime[198] to give colored complexes which can be extracted into an organic solvent prior to the spectrophotometric determination.

Nioxime and α-furildioxime[199] have been proposed as reagents for the spectrophotometric determination of Ni-Fe, Ni-Re, and Cu-Fe mixtures.

Nickel nioxime can be collected at the interface by shaking the aqueous phase with an organic solvent. This scheme has been used to separate nickel from 30,000 times as much cobalt[200].

The 4-isopropylnioxime method for nickel[189], the 4-methylnioxime method for palladium[191], and the 4-methylnioxime method for rhenium[198] are recommended.

D. Titrimetric Methods

Holluta[201] titrated the acid liberated when a solution containing nickel was treated with dimethylglyoxime. Tougarinoff[202] precipitated nickel with dimethylglyoxime, dissolved the precipitate in hot acid and titrated the resulting hydroxylamine with potassium permanganate. Mironoff[203] used the Tougarinoff procedure for the determination of nickel and copper with α-benzildioxime. Ishibashi and Tetsumoto[204] titrated nickel with dimethylglyoxime using iron(III) as an external indicator. Hooker and Banks[120] titrated nickel with 4-isopropylnioxime in a chloroform (20%)-water (20%)-methanol (60%) mixture and determined the end point spectrophotometrically. Fritz[205] dissolved nickel dimethylglyoxime in glacial acetic acid and titrated the resulting acetate ions with perchloric acid in acetonitrile media. Bobtelsky and Welwart[206] titrated nickel with dimethylglyoxime and determined the end point by means of a photoelectric titrimeter.

E. Polarographic Methods

Nickel has been determined by amperometric titration with dimethylglyoxime[207] and nioxime[208-211]. Cobalt has also been determined by amperometric titration with nioxime[210]. Nickel has been determined by measuring the associated nioxime by polarographic means[212].

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