valid for the chlorides[23] of all the other rare earths which will fit inside the ice III hole and for any smaller trivalent ions, provided no hydrolysis occurs. These models satisfy all the necessary criteria mentioned at the beginning and are consistent with all the other evidence presented above. However, lower valence types with a weaker coulombic interaction will pull in the solvent to a somewhat lesser extent, and larger ions may badly distort the configurations. As a result the symmetry and structure may well be different in these cases.[24]

It cannot be claimed that the structures proposed *must* be the actual ones present, but they seemed to be the most probable ones consistent with the currently available information.

Acknowledgments.—The author wishes to acknowledge the very considerable contributions of Dr. E. V. Sayre of Brookhaven National Laboratory to this discussion. The above notions are the result of an extended interchange of ideas with Dr. Sayre on various possible models consistent with the spectra. The author also wishes to thank Drs. Simon Freed, Allan Zalkin and Donald Sands for their aid in various aspects of this investigation.

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[23] The bromides, iodides, perchlorates, etc., should be similar to the chloride. However, the spectrum of aqueous $Eu(NO_3)_3$,[5] for example, shows that some sort of complexing or ion association occurs, and in such circumstances these models will not apply.

[24] Thus in an (unpublished) experiment on alcoholic solutions of $PrCl_3$, E. V. Sayre and D. G. Miller have found that *two* distinct solvate configurations are frozen out at liquid helium temperature. The Pr^{+3} ion has a larger ionic radius (1.00 Å.) than Eu^{+3}, and thus might be too large for the proposed configurations. Unfortunately, the lines were too broad for any detailed electric field symmetry analysis.

LIVERMORE, CALIF.

[CONTRIBUTION NO. 580 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Intermolecular Metal–Metal Bonds and Solubility of Some Nickel and Palladium Complexes of *vic*-Dioximes[1]

BY CHARLES V. BANKS AND DENNIS W. BARNUM[2]

RECEIVED JANUARY 11, 1958

The effect of the strength of intermolecular metal–metal bonds on the solubility of twelve nickel(II) and palladium(II) complexes of *vic*-dioximes was studied. Metal–metal bond lengths were measured in the nickel and palladium complexes of dimethylglyoxime, nioxime, heptoxime, α-furildioxime, α-benzildioxime and in nickel 3-methylnioxime and nickel 4-methylnioxime. All of these complexes, except palladium heptoxime, have the same crystal structure as nickel dimethylglyoxime. Palladium heptoxime still has a structure containing metal chains. Molar solubilities in water, chloroform and 1,2-dichlorobenzene are compared with the metal–metal bond lengths. No correlation was found because of the wide variation in the nature of the ligands. The solubility products of the nickel(II) complexes of dimethylglyoxime, nioxime, 4-methylnioxime, 3-methylnioxime and heptoxime were measured at 25.0° and at 40.0°. Values of ΔF^0, ΔH^0 and ΔS^0 were calculated. Excluding nickel dimethylglyoxime, the solubility product increases with increasing metal–metal bond length. The solubility product of nickel dimethylglyoxime seems to be unusually large and shows that this product depends on the nature of the ligand as well as on the metal–metal bond length.

Introduction

Godycki and Rundle[3] have determined the crystal structure of nickel dimethyglyoxime. They found that the square planar molecules are 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. They proposed that weak intermolecular nickel–nickel bonds exist, thus forming a chain of nickel atoms that is responsible for the well known selectivity of dimethylglyoxime as a gravimetric reagent for nickel(II) and palladium(II). Copper dimethylglyoxime, which has almost identically the same molecular structure as nickel dimethylglyoxime but packs differently in the crystal so that no –Cu–Cu– bonds are possible, is soluble in water. Thus, the metal chains contribute enough stability to the crystal of nickel dimethylglyoxime so that it is insoluble in water and the unique packing tends to prevent coprecipitation. On the basis of the relative solubilities of nickel dimethylglyoxime and copper dimethylglyoxime, Rundle[4] has estimated that the metal chains in the nickel complex contribute about 10 kcal./mole to the stability of the crystal.

The existence of metal–metal interaction in nickel dimethylglyoxime has been confirmed by Yamada and Tsuchida[5] from measurements of the dichroism of the nickel, platinum and copper complexes of dimethylglyoxime. It also has been shown that the Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$, and the complex $[Au^{III}(DH)_2][Au^{I}Cl_2]$ (where DH^- is the anion of dimethylglyoxime) contain chains of metal–metal bonds of comparable length,[4,6,7] and that other *vic*-dioxime[8] complexes of nickel, palladium and platinum have the same structure as nickel dimethylglyoxime.[3,9,10]

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[1] No. XXI in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XX, *J. Org. Chem.*, in press (1958). Abstracted from dissertation submitted by Dennis W. Barnum to graduate faculty of Iowa State College in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1957.

[2] Shell Development Co., Emeryville, Calif.

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

[4] R. E. Rundle, THIS JOURNAL, **76**, 3101 (1954).

[5] S. Yamada and R. Tsuchida, *ibid.*, **75**, 6351 (1953).

[6] S. Yamada, *ibid.*, **73**, 1579 (1951).

[7] M. Atoji, J. W. Richardson and R. E. Rundle, *ibid.*, **79**, 3017 (1957).

[8] The prefix *vic-* is an abbreviation for *vicinal*, and a *vic*-dioxime is one in which the oxime groups are on adjacent carbon atoms. Nioxime and heptoxime are the trivial names for 1,2-cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime, respectively.

[9] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

[10] J. Pech, M. Polster and A. Rezabek, *Chem. Listy*, **43**, 180 (1949); *C. A.*, **44**, 9295c (1950).

The nature of the bonding in intermolecular metal–metal bonds is discussed by Godycki and Rundle[3] and by Rundle.[11]

If metal–metal bonding is responsible for the insolubility of nickel dimethyglyoxime, one might expect to observe an increase in solubility in a series of complexes in which the metal–metal bond becomes longer and longer. With this view in mind Hooker[12,13] prepared a series of nickel complexes of substituted nioximes in which the bulkiness of the *vic*-dioxime was taken as a rough measure of the metal–metal bond length. Although the results of this work were inconclusive, there was some indication that the solubility in chloroform and the color of the solid complex may depend on the metal–metal bond length.

While the present work was in progress Sharpe and Wakefield[9] published a paper in which they conclude that the molar solubility in water does depend on the metal–metal bond length. However, we conclude that the solubility depends on the nature of the ligand as well as on the metal–metal distance, and, in fact, the effect of the ligand may be so great that it completely overshadows the effect of the metal chains.

In this work, the metal–metal bond lengths in several nickel(II) and palladium(II) complexes were measured accurately and compared with the solubility products in water and the molar solubilities in water, chloroform and 1,2-dichlorobenzene.

Experimental

Growth of Crystals.—Crystals of suitable size for X-ray measurements were prepared by very slow crystallization from organic solvents. Nitrobenzene, 1,2-dichlorobenzene and trichloroethylene were found to give the largest crystals.

Crystals of nickel diaminoglyoxime were prepared by homogeneous precipitation from urea solution at 45°. About 2–3 weeks are required to grow crystals of appropriate size.

Measurement of Metal–Metal Bond Lengths.—The metal–metal bond lengths were obtained from the lattice constant, *c*, by simple application of the Bragg equation. The back reflection Weissenberg technique was used which allows one to eliminate certain systematic errors. This technique is discussed in detail by Buerger.[14] It was found that the function $\cot\theta\cos^2\theta$ came the closest to giving a straight line extrapolation.

Single crystals of nickel 3-methylnioxime and nickel 4-methylnioxime suitable for X-ray measurements could not be obtained. The metal–metal bond lengths in these complexes were determined from powder photographs. In the other complexes the bond lengths calculated from powder photographs were compared with those obtained from back reflection measurements of single crystals and it was found that the values from the powder method are accurate to about ±0.03 Å.

Measurement of Solubility in Organic Solvents.—Saturated solutions were prepared either by shaking an excess of the solid with a few milliliters of the solvent for three days or by preparing a hot saturated solution and allowing this to stand at 25° for three days. The excess solid was filtered off, taking care to keep evaporation of the solvent to a minimum. An aliquot of the filtrate was diluted to a convenient concentration to measure the absorbancy with a Beckman DU spectrophotometer. The solubility was then calculated from the known molar absorptivity.

Measurement of Solubility Products.—The solubility product of nickel dimethylglyoxime at 25° was measured by Christopherson and Sandell[15] and by Babko and Mikhelson[16] by determining the solubility of the nickel complex in acidic solutions. However, at 40° it was found that appreciable hydrolysis of heptoxime and nioxime would occur before a saturated solution was obtained. Decreasing the acidity in order to prevent acid hydrolysis of the *vic*-dioxime seemed to increase the time required to attain solubility equilibrium, and measurement of the solubility products in solutions saturated with nioxime or heptoxime is not practical since the concentration of nickel ions is reduced to about 10^{-9} mole/l.

Wenger, Monnier and Bachmann-Chapuis[17] measured the solubility product of nickel nioxime at 25° by determining the *p*H at which the complex just begins to precipitate from an acidic solution. This method was tried for nickel dimethylglyoxime, nickel nioxime and nickel heptoxime. In ten determinations of each constant the solubility products varied over a range as great as 100 units. It was found that the value obtained depends upon the rate of addition of the sodium hydroxide and the color one takes for the end-point.

A new method was devised for measuring the solubility products of these complexes in which the nickel chloride and the *vic*-dioxime are simply mixed in stoichiometric amounts at the desired temperature, shaken for 2 hr. and the *p*H measured.

In this method the nickel chloride solution used was 0.0229 *M*, the nioxime, 3-methylnioxime and 4-methylnioxime solutions were 0.0458 *M*, the heptoxime solution was 0.0229 *M*, and the dimethylglyoxime solution was 0.00229 *M*. Enough of the *vic*-dioxime solution was taken, by means of a micro-pipet, to react with between 0.100 and 1.00 ml. of the nickel chloride solution. A known amount of water was then added to bring the total volume to about 20 ml. and the solution placed in the constant temperature bath. After temperature equilibrium was reached, the desired amount of nickel chloride solution was added. The mixture was shaken for at least 2 hr., and then, without filtering, the *p*H was measured with a Beckman Model G *p*H meter.

Starting with equations 1, 2, 3 and 4 it is possible to derive an expression for the solubility product.

$$m_{\mathrm{Ni}} = c_{\mathrm{Ni}^{++}} + c_{\mathrm{Ni(DH)_2}} \qquad (1)$$

$$m_{\mathrm{DH_2}} = c_{\mathrm{DH}^-} + c_{\mathrm{DH_2}} + 2c_{\mathrm{Ni(DH)_2}} \qquad (2)$$

$$c_{\mathrm{H}^+} + 2c_{\mathrm{Ni}^{++}} = c_{\mathrm{Cl}^-} + c_{\mathrm{DH}^-} \qquad (3)$$

$$K_{\mathrm{DH_2}} = \frac{a_{\mathrm{H}^+}a_{\mathrm{DH}^-}}{a_{\mathrm{DH_2}}} \qquad (4)$$

$$K_{\mathrm{sp}} = a_{\mathrm{Ni}^{++}}a^2_{\mathrm{DH}^-} \qquad (5)$$

The equation for the solubility product is then

$$K_{\mathrm{sp}} = \frac{K^2_{\mathrm{DH_2}}f^2_{\mathrm{DH_2}}}{a^2_{\mathrm{H}^+}}\left[m_{\mathrm{Ni}}f_{\mathrm{Ni}^{++}} - \frac{a_{\mathrm{H}^+}f_{\mathrm{Ni}^{++}}}{2f_{\mathrm{H}^+}}\right]\left[2m_{\mathrm{Ni}} - \frac{a_{\mathrm{H}^+}}{f_{\mathrm{H}^+}}\right]^2 \qquad (6)$$

In the above equations, m_i is the total amount of an atom or group of atoms, regardless of the species in which it exists, expressed in mole per liter, c_i is the molar concentration of species i, and f_i is the molar activity coefficient of species i. Values of the activity coefficients were calculated from the second approximation to the Debye–Hückel equation

$$\log f_i = -\frac{Az^2_i\sqrt{\mu}}{1 + \alpha_i B\sqrt{\mu}} \qquad (7)$$

Values of *A* and *B* for molar activity coefficients were taken from Bates[18] and values of α_i from the data presented by Kielland.[19]

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(11) R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957).

(12) D. T. Hooker, "Preparation, Properties and Analytical Applications of some Substituted Alicyclic *vic*-Dioximes," unpublished Ph.D. thesis, Iowa State College, Ames, Iowa, 1955.

(13) C. V. Banks, D. T. Hooker and J. J. Richard, *J. Org. Chem.*, **21**, 547 (1956).

(14) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942.

(15) H. Christopherson and E. B. Sandell, *Anal. Chim. Acta*, **10**, 1 (1954).

(16) A. K. Babko and P. B. Mikhelson, *Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **5**, [8] 61 (1954).

(17) P. E. Wenger, D. Monnier and W. Bachmann-Chapuis, *Anal. Chim. Acta*, **15**, 473 (1956).

(18) R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954.

(19) J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

At 25° the first ionization constants, K_{DH_2}, of dimethylglyoxime, nioxime and heptoxime are known from the work of Banks and Carlson.[20] Values of these constants at 40° were measured in the course of this work.

In all the methods for measuring the solubility products, the presence of the species $Ni(DH)^+$ was neglected. An equation for the solubility product, taking the presence of this species into account, was derived. By substituting actual data into this equation, it was shown that in the case where this species would have the greatest effect the stability constant would have to be smaller than 10^{10} in order to affect the solubility product by 1%. Charles and Freiser[21] report a value of 2.76×10^{10} in 50% dioxane–water solution at 25°, and their data show that this constant does not change appreciably between 25 and 40°. In pure water one would expect this constant to be somewhat smaller. Thus, it appears that a small correction might be necessary in a very accurate determination. In the present measurements it is in all probability less than experimental error.

Measurement of Ionization Constants.—The acid dissociation constants of dimethylglyoxime, nioxime and heptoxime were measured at 40° using the method previously employed by Christopherson and Sandell[15] and by Babko and Mikhelson.[22]

Sodium bicarbonate–sodium hydroxide buffer solutions ranging in *p*H from 9.60 to 11.00 were prepared by the method of Bates and Bower.[23] For dimethylglyoxime, 100 ml. of buffer was added to an excess of the solid *vic*-dioxime in a 200-ml. volumetric flask. For nioxime and heptoxime, 50 ml. of buffer solution was added to the excess solid. The mixture was placed on a mechanical shaker and maintained at 40.0° for 2 hr. Still keeping the solution at 40.0°, the excess solid was filtered off, the *p*H measured and an aliquot of the filtrate taken with a pipet. The aliquot was diluted to about 250 ml. and the *vic*-dioxime determined gravimetrically by precipitating it as the nickel complex. The pipets were calibrated for delivery of solution at 40°, and it was found that no correction was necessary.

It can be shown easily that the solubility, S, is given by

$$S = c_{DH_2} + \frac{K_{DH_2}c_{DH_2}}{a_{H^+}f_{DH^-}} \qquad (8)$$

Therefore, a plot of solubility against $1/(a_{H^+}f_{DH^-})$ should give a straight line of slope equal to $K_{DH_2}c_{DH_2}$ and intercept equal to c_{DH_2}. A straight line actually was obtained, indicating that in the *p*H range used there is no noticeable formation of the doubly ionized $D^=$ ion.

The ionic strength of the buffer saturated with a *vic*-dioxime is different from that of the original buffer. For a first approximation, the ionic strength was taken as equal to that of the original buffer. A second approximation was then made by calculating the concentration of each ionic species present. In two of the most concentrated solutions encountered a third approximation of μ gave no improvement over the second.

Table I gives the values of the ionization constants used in this work.

TABLE I

FIRST IONIZATION CONSTANTS OF SOME *vic*-DIOXIMES

vic-Dioxime	25°	40°
Dimethylglyoxime	2.5×10^{-11}	3.0×10^{-11}
Nioxime	2.5×10^{-11}	3.1×10^{-11}
Heptoxime	2.0×10^{-11}	3.4×10^{-11}

The ionization constants of 3-methylnioxime and 4-methylnioxime were not determined. It was assumed that they are the same as those of nioxime itself. In view of the close agreement of the constants in Table I, this should be a valid assumption.

Results and Discussion

Crystal Structure.—All of the complexes listed in Table II, except palladium heptoxime, have the same crystal structure as nickel dimethylglyoxime. The X-ray diffraction pattern of palladium heptoxime shows that it has a lower symmetry. However, the dichroism of the crystal and comparison of the absorption spectra of the complex in colloidal suspension and in chloroform solution indicate the presence of metal chains.[24] Comparison of the –Ni–Ni– bond lengths with the –Pd–Pd– bond lengths also shows that in palladium heptoxime this bond is shorter than would be expected if it had the same structure as nickel dimethylglyoxime. It is believed that adjacent molecules along the metal chain are no longer rotated exactly 90° with respect to one another as they are in nickel dimethylglyoxime but through some smaller angle that permits a shorter metal–metal bond.

TABLE II

METAL–METAL BOND LENGTHS AND SOLUBILITIES AT 25° OF SOME NICKEL AND PALLADIUM COMPLEXES OF *vic*-DIOXIMES

Complex	–M–M– bond length, Å.	Sol. in $CHCl_3$ $\times 10^4$, mole/l.	Sol. in 1,2-dichlorobenzene $\times 10^4$, mole/l.	Sol. in water $\times 10^6$, mole/l.
Nickel dimethylglyoxime	3.233	5.5	2.0	2.1
Nickel nioxime	3.237	0.67	0.32	1.6
Nickel α-furildioxime	3.448	16	18	0.63
Nickel α-benzildioxime	3.547	13	5.9	0.70
Nickel heptoxime	3.596	56	13	0.90
Nickel 4-*t*-amylnioxime[a]	3.2	...	...	..
Nickel 4-isopropylnioxime	3.19	...	...	..
Nickel 3-methylnioxime	3.47	...	...	..
Nickel 4-methylnioxime	3.24	...	...	..
Palladium dimethylglyoxime	3.253	5.0	...	..
Palladium nioxime	3.250	1.4	...	..
Palladium α-furildioxime	3.459	8.1	...	..
Palladium α-benzildioxime	3.517	8.5	...	..
Palladium heptoxime[b]	3.329	89	...	..

[a] The X-ray powder pattern of nickel 4-*t*-amylnioxime shows rather diffuse lines, probably due to the presence of *cis* and *trans* isomers about the nickel atom. [b] Palladium heptoxime has a slightly different structure than the other complexes. See text.

Nickel diaminoglyoxime crystallizes with an entirely different structure that does not contain metal chains. The crystal shows practically no dichroism. It is insoluble in all common organic solvents except dimethylformamide and glacial acetic acid, which indicates that it forms a more stable crystal than nickel dimethylglyoxime.

Metal–Metal Bond Lengths.—The metal–metal bond lengths in several complexes are recorded in Table II. One will notice that there is a rather large spread between the shortest and the longest bond, 3.2 to 3.6 Å.

One would expect the metal–metal distance to depend on the bulkiness of the ligand. Except for nickel 4-*t*-amylnioxime and nickel 4-isopropylnioxime this seems to be the case. It can be shown

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[20] C. V. Banks and A. B. Carlson, *Anal. Chim. Acta*, **7**, 291 (1952).

[21] R. G. Charles and H. Freiser, *ibid.*, **11**, 101 (1954).

[22] A. K. Babko and P. B. Mikhelson, *Zhur. Anal. Khim.*, **6**, 167 (1951).

[23] R. G. Bates and V. E. Bower, *Anal. Chem.*, **28**, 1322 (1956).

[24] See following paper by C. V. Banks and D. W. Barnum, THIS JOURNAL, **80**, in press (1958).

by means of Fisher–Hirschfelder–Taylor models that an isopropyl group or a *t*-amyl group can be accommodated in the 4-position in two ways. In one way the group would present a great deal of steric hindrance to metal–metal bonding, and in the other way it would present little more hindrance than in nioxime itself. Apparently only molecules of the latter sort are present in the crystals, and the metal–metal bond length is shorter than in nickel nioxime because of additional van der Waals attraction due to the alkyl substituents.

A similar situation exists in the 3-position. In one configuration the hindrance to metal–metal bond formation is far greater than in the other. Furthermore, one would expect that a substituent in the 3-position would have a far greater influence on the metal–metal bond length than the same group in the 4-position. The bond lengths in nickel 3-methylnioxime and nickel 4-methylnioxime bear this out.

Solubilities in Organic Solvents.—The solubilities of some of the complexes in chloroform and in 1,2-dichlorobenzene are listed in Table II. It is obvious that the solubility in organic solvents depends on factors other than the metal–metal bond length. This is not surprising in view of the wide variation in the nature of the ligands. If one may compare nickel nioxime and nickel heptoxime, in which the ligands are very similar, one sees that the solubility does increase with increasing metal–metal bond length. On the other hand, nickel nioxime and nickel 4-methylnioxime have very similar ligands and practically the same metal–metal bond length, but the methyl substituted complex is about 600 times more soluble in chloroform.

Solubilities in Water.—In Table II the solubilities of some nickel complexes in water are compared with the nickel–nickel bond lengths. Upon comparing these data with the metal–metal bond lengths, it is evident that there is no direct correlation. This result is in contradiction to the conclusion of Sharpe and Wakefield[9] that the solubility increases as the length of the metal–metal bond increases.

Solubility Products, Heats of Solution and Entropy Changes.—From the solubility products at 25 and 40°, values of ΔF^0, ΔH^0 and ΔS^0 were calculated. These data are listed in Table III for the reaction

$$\mathrm{Ni(DH)_2(c) = Ni^{++}(aq.) + 2DH^-(aq.)} \qquad (9)$$

For the solubility product of nickel dimethylglyoxime, Christopherson and Sandell[15] obtained the value 1.8×10^{-24} at 25°, and Babko and Mikhelson[16] obtained 2×10^{-25} (temperature not given). In both cases a slightly different value of the ionization constant of dimethylglyoxime was used. When these data are recalculated, using the same dissociation constant as was used in this work, agreement is very good.

Wenger, Monnier and Bachmann-Chapuis[17] report two values of the solubility product of nickel nioxime at 25°: 10^{-27} from the *p*H at which the complex just begins to precipitate and 10^{-30} from polarographic measurements. We have found the first method to be very inaccurate. Agreement with the latter value is not intolerable.

TABLE III

THERMODYNAMIC CONSTANTS FOR THE REACTION $\mathrm{Ni(DH)_2(c) = Ni^{++}(aq) + 2DH^-(aq)}$

Complex	–M–M– bond length, Å.	T, °K.	K_{sp}	ΔF^0, kcal.	ΔH^0, kcal.	ΔS^0, e.u.
Nickel dimethylglyoxime	3.233	298	2.2×10^{-24}	32.15	12	−67
		313	5.9×10^{-24}	33.15		
Nickel nioxime	3.237	298	4.1×10^{-29}	38.58	41	+ 7.3
		313	1.1×10^{-27}	38.47		
Nickel 4-methylnioxime	3.24	298	5.6×10^{-29}	38.39	29	−29
		313	6.3×10^{-28}	38.82		
Nickel 3-methylnioxime	3.47	298	2.4×10^{-28}	37.53	26	−37
		313	2.1×10^{-27}	38.09		
Nickel heptoxime	3.596	298	2.3×10^{-27}	36.20	25	−36
		313	1.8×10^{-26}	36.74		

Excluding nickel dimethylglyoxime, one sees in Table III that at constant temperature an increase in the length of the metal–metal bonds is accompanied by an increase in the solubility product. In this series the ligands are very similar. Their molecular weights are very close and the oxime groups are attached to a six or seven-membered ring.

Nickel dimethylglyoxime, however, has almost exactly the same –Ni–Ni– bond length as nickel nioxime yet its solubility product is greater by a factor of 5.4×10^4. Writing the dissolution process as

$$\mathrm{Ni(DH)_2(c)} \xrightleftharpoons{K_1} \mathrm{Ni(DH)_2(aq.)} \xrightleftharpoons{K_2} \mathrm{Ni^{++}(aq.) + 2DH^-(aq.)}$$

one sees that the solubility product depends on the instability constant for the nickel complex and on the intrinsic solubility, *i.e.*, $K_{sp} = K_1K_2$. Thus the difference between the solubility products of nickel dimethylglyoxime and nickel nioxime might be due to a radical difference in the instability constants rather than in the lattice energy of the crystals.

In Table III, values of ΔH^0 and ΔS^0 for the dissolution process are reported. It will be noted that the values for nickel dimethylglyoxime are very different compared with the other complexes.

The negative values of ΔS^0 are, no doubt, due to solvation of the nickel ion. Charles and Freiser[21] obtained the value −106 e.u. for the reaction

$$\mathrm{Ni(DH)_2(aq.) = Ni^{++}(aq.) + 2DH^-(aq.)}$$

in 50% dioxane–water. They attributed this to the over-all decrease in the number of particles due to solvation.

Acknowledgments.—The authors are indebted to R. E. Rundle for his help in measuring the metal–metal bond lengths and for many helpful discussions. We also wish to thank J. P. LaPlante for preparing the crystals of diaminoglyoxime.

AMES, IOWA