

In the early phases of this study it was anticipated that the complexity constants of the copper complexes could be calculated by correcting the pyrophosphate concentration for that lost through simple complex formation with the alkali metal ions. Such a procedure would be valid only if no complexes of the type $\text{Na}_x\text{Cu}(\text{P}_2\text{O}_7)_2^{(6-x)-}$ were formed. On the basis of this assumption the presence of increasing concentrations of alkali metal ions should have decreased the potential shift. Instead, the presence of up to 0.1 M Cs^+ , K^+ , and Na^+ enhanced the potential shift as much as 10 mv. in the more alkaline solutions. In the presence of lithium ions, the voltage shift due to complex formation was enhanced only slightly from a pH of 5 to 8 and was greatly reduced above pH 8. These results constitute good evidence that the copper pyrophosphate complexes also associate with alkali metal ions, which enhances the stability of the complex $\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}$ which is predominant in the more alkaline solutions. The effect is too large to be due to activity effects but is too small to permit a calculation of the extent of association. It is possible that the alkali

metal ions are held by loose ion-pair bonds at the outer surface of the complex. Their presence could enhance the stability of the complex by a reduction of the repulsive forces of the two negatively charged pyrophosphate ions which surround the copper(II) ion. Since the strength of the bond with alkali metal ions increases with decreasing ionic radii it is possible that lithium ions not only decrease the repulsive forces but weaken the copper(II) pyrophosphate bond in the same manner as do hydrogen ions. If the apparent acidity constants, measured in the same supporting electrolyte and the same concentrations, are used to calculate the concentrations of $\text{P}_2\text{O}_7^{4-}$, $\text{HP}_2\text{O}_7^{3-}$, and $\text{H}_2\text{P}_2\text{O}_7^{2-}$ ions and any association with alkali metals is disregarded, the values obtained for the stability constants of the copper complexes agree reasonably well with those obtained in the absence of alkali metal ions. Their use in practical situations under similar experimental conditions thus is justified.

Acknowledgment.—This work was supported in part by a General Electric Foundation Fellowship granted to P. E. S.

CONTRIBUTION NO. 1134 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA^{1a}

Stability Constants and Intrinsic Solubility of Several Nickel(II)-*vic*-Dioxime Complexes^{1b}

BY CHARLES V. BANKS AND SAMUEL ANDERSON

Received March 15, 1962

The acid dissociation constants for a series of *vic*-dioximes and the stability constants of their nickel(II) complexes were measured in dioxane-water mixtures. Estimates are given for the values of the acid dissociation constants and stability constants in water solution. The solubility product constants for the nickel(II)-*vic*-dioxime complexes were measured in water solution. The stability constants and the solubility product constant were used to calculate the intrinsic solubility. It was found that, in general, an increase in the distance between nickel atoms in the crystal of the complexes results in an increase in the solubility of the complexes. It is believed that the phenomena above may be accounted for in part by metal-metal bonding in some of the nickel(II)-*vic*-dioxime complexes.

Introduction

Several quite insoluble nickel(II)-,² palladium(II)-,^{2,3} and platinum(II)-*vic*-dioxime⁴ complexes have been shown to have, in general, the same crystal structure as does nickel dimethylglyoxime,⁵ $[\text{Ni}(\text{DMG})_2]$. This rather unique crystal structure in which the metal

atoms lie in a straight row extending throughout the length of the crystal led Godycki and Rundle⁵ to postulate the presence of metal-metal bonding which could contribute significantly to the crystal energy and thus perhaps explain the limited solubility of these complexes. The fact that nickel(II)-ethylmethylglyoxime,⁶ $[\text{Ni}(\text{EMG})_2]$, and copper(II)-dimethylglyoxime,⁷ $[\text{Cu}(\text{DMG})_2]$, are much more soluble in water than is $\text{Ni}(\text{DMG})_2$ and that both have crystal structures which are not compatible with metal-metal bonding lends support to this postulate. Banks and Anderson⁸ measured the heats of solution of $\text{Ni}(\text{DMG})_2$ and $\text{Ni}(\text{EMG})_2$ in both *n*-heptane and carbon tetrachloride and found ΔH^0 was about 10 kcal. greater for $\text{Ni}(\text{DMG})_2$ than

(1) (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Paper No. XXXI in a series on "Chemistry of the *vic*-Dioximes." Previous papers in this series were No. XXVIII, "Proceedings of the Symposium," Feigl Anniversary Symposium, Birmingham Univ., Birmingham, England, April 9-13, 1962; No. XXIX, *J. Am. Chem. Soc.*, **84**, 1486 (1962); and No. XXX, *J. Phys. Chem.* (Feb., 1963). Abstracted from dissertation submitted by Samuel Anderson to graduate faculty of Iowa State University in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1962.

(2) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 3579 (1958).

(3) C. Panattoni, E. Frasson, and R. Zannetti, *Gazz. chim. ital.*, **89**, 2132 (1959).

(4) E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, **12**, 1027 (1959).

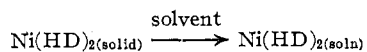
(5) L. E. Godycki and R. E. Rundle, *ibid.*, **6**, 487 (1953).

(6) E. Frasson and C. Panattoni, *ibid.*, **13**, 893 (1959).

(7) E. Frasson, R. Bardi, and S. Bezzi, *ibid.*, **12**, 201 (1959).

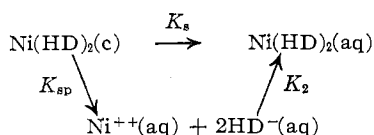
(8) C. V. Banks and S. Anderson, *J. Am. Chem. Soc.*, **84**, 1486 (1962).

for Ni(EMG)₂ according to the reaction



where HD⁻ represents the singly ionized species of any of the *vic*-dioximes. This difference in the stabilities of the crystals was largely attributed to nickel-nickel bonding in Ni(DMG)₂.

If, indeed, the presence of nickel-nickel bonds contributes significantly to the stability of the crystals, one might reasonably expect a correlation to exist between the nickel-nickel bond length and the intrinsic solubility, K_s , the solubility product constant, K_{sp} , or the over-all stability constant, K_2



Banks and Barnum² suggested that the limited correlation which they found between the Ni-Ni bond length and the solubility product constant might be attributed to the ligand effect. For this reason, it was felt that the intrinsic solubility, which should be less dependent on the ligand effect than K_{sp} , might correlate rather well with the Ni-Ni bond lengths.

Experimental

The values of the over-all stability constants, K_1 and K_2 , were determined from the formation function.⁹

However, the low solubility of the nickel(II)-*vic*-dioximes in water made it desirable to use mixtures of water and organic solvents to determine their stability. The relationship between the stability of metal-ligand complexes in water solution and in organic solvent-water mixtures has been investigated by Irving and Rossotti.¹⁰ They have shown that eq. 1 expresses approximately this relationship.

$$\log K_1 = \log \bar{K}_1 - (p\bar{K}_{a_1} - p\bar{K}_{a_2}) \quad (1)$$

where K_1 represents the constant in water and \bar{K}_1 represents the constant in the mixed solvent. This same symbolism will be used for all equilibrium constants discussed in this work.

Equation 1 applies only to the stability of the 1:1 complex but approximations for $1/2 \log K_2$ can be obtained by using $1/2 \log \bar{K}_2$.

Apparatus and Reagents.—The pH measurements were made at 25° with a Beckman Model G pH meter using Beckman Type E glass and Beckman No. 1190-80 calomel electrodes. The pH meter was calibrated with Beckman buffers (pH 4.01, 7.00, 9.18). Rapid mixing of solutions was achieved by means of a magnetic stirrer which was stopped during the actual pH measurements.

Dimethylglyoxime was obtained from the Matheson Company.

Nioxime¹¹ (cyclohexanedionedioxime); heptoxime¹² (cycloheptanedionedioxime); 3-methylnioxime, 4-methylnioxime, and 4-isopropylnioxime¹³; and diethylglyoxime and di-*n*-propylglyoxime¹⁴⁻¹⁶ were prepared by published procedures. Each of the

vic-dioximes was recrystallized at least three times from alcohol-water mixtures and dried in a vacuum oven at 40° before use.

A standard solution of nickel(II) perchlorate was prepared by dissolving Mond nickel in aqua regia, evaporating to near dryness with perchloric acid, diluting, and standardizing by precipitation with dimethylglyoxime. The sodium perchlorate and sodium hydroxide were of reagent grade.

The dioxane was purified by using the method described by Vogel.¹⁷

Cobalt(II) and copper(II) solutions were standardized by titrating with standard ethylenediaminetetraacetic acid.

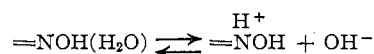
\bar{n} - and [HD⁻] Values.—The values of \bar{n} and [HD⁻] were determined at an ionic strength of 0.1 in 75% dioxane-25% water (v./v.) mixtures, which were chosen because they dissolved all of the nickel(II)-*vic*-dioxime complexes studied.

The experimental procedures for the titrations have been described by Charles and Freiser.¹⁸ The change in ionic strength due to addition of base and dioxane was about 7%. According to Ringbom,¹⁹ the corrections to be applied for change in activity coefficients can be neglected for solutions which have an ionic strength of the order of 0.1 or higher, provided the volume change is small. The hydrolysis of the nickel(II) ion is not appreciable at the pH values used in this study.²⁰ No precipitation of the metal-ligand complex occurred during any of the titrations except for nickel(II)-nioxime mixtures. Data taken after precipitation had occurred were not used in the calculations.

$p\bar{K}_{a_1}$ and $p\bar{K}_{a_2}$ Values.—The first acid dissociation constants of the various *vic*-dioximes were measured in dioxane-water mixtures by titration with sodium hydroxide solutions under the same conditions used for titrating the metal and the ligand. In order to avoid the replacement of more than one of the dioxime hydrogens, only about 0.1 mole of base per mole of *vic*-dioxime was added. During the titration, increments of dioxane were added in order to keep the dioxane content constant. Nitrogen, saturated with water vapor, was passed over the solution during the titration.

The acid dissociation constants of the *vic*-dioximes in water were determined by measurements in several concentrations of dioxane. The $p\bar{K}_{a_1}$ was plotted against the percentage of dioxane and extrapolated to zero concentration of dioxane. Linear functions were obtained for all the *vic*-dioximes studied (Fig. 1 and 2).

$p\bar{K}_b$ Values.—The $p\bar{K}_b$ (basicity of the oxime nitrogen) was determined in dioxane-water mixtures for each *vic*-dioxime



studied by titrating a known amount of *vic*-dioxime with a standard acid solution. In all cases, the $p\bar{K}_b$ was approximately 16, which indicated negligible basicity of the oxime nitrogen.

Calculation of $\log \bar{K}_1$ Values.—The equilibrium constants are given in Table I. Many values for the stability constants were calculated by using appropriately selected pairs of \bar{n} and [HD⁻] values. The data were programmed for an IBM 650 using the procedure of Wolontis.²¹

Calculation of $\log K_1$ Values.—Values for $\log K_1$ and $1/2 \log K_2$ were calculated from the corresponding values for $\log \bar{K}_1$ and $1/2 \log \bar{K}_2$ by means of eq. 1. In order to show that eq. 1 gives a good approximation for the stability constant of Ni-(DMG)₂ in water solution, the stability constants of Cu(DMG)₂ and Co(DMG)₂ were determined in water, in 50% dioxane-water (v./v.), and in 75% dioxane-25% water (v./v.) mixtures. Thus, a comparison of the values of ($p\bar{K}_{a_1} - p\bar{K}_{a_2}$) for dimethylglyoxime as determined experimentally and as determined from the stability constants of Cu(DMG)₂ and Co(DMG)₂ in water

(9) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(10) H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).

(11) C. C. Hach, C. V. Banks, and H. Diehl, *Org. Syn.*, **32**, 35 (1952).

(12) R. W. Vander Haar, R. C. Voter, and C. V. Banks, *J. Org. Chem.*, **14**, 836 (1949).

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

(14) J. M. Snell and S. M. McElvain in "Organic Syntheses," Collective Volume II, John Wiley and Sons, New York, N. Y., 1943, p. 114.

(15) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 111 (1946).

(16) W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).

(17) A. I. Vogel, "A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948.

(18) R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 101 (1954).

(19) A. Ringbom, *J. Chem. Educ.*, **35**, 282 (1958).

(20) F. Achenza, *Ann. chim. (Rome)*, **49**, 624 (1959).

(21) V. M. Wolontis, International Business Machines Corporation Technical Newsletter, No. 11, 1956.

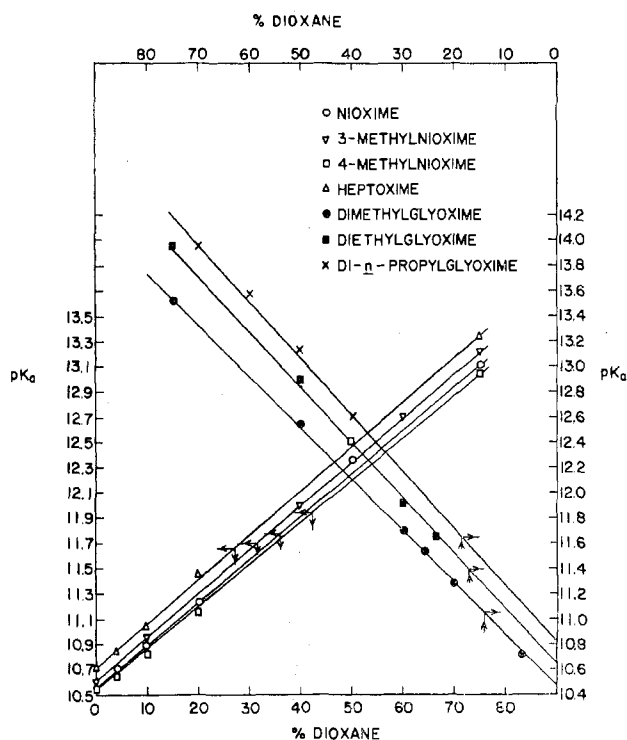


Fig. 1.—Plot of negative logarithm of acid dissociation constant against % dioxane for several *vic*-dioximes.

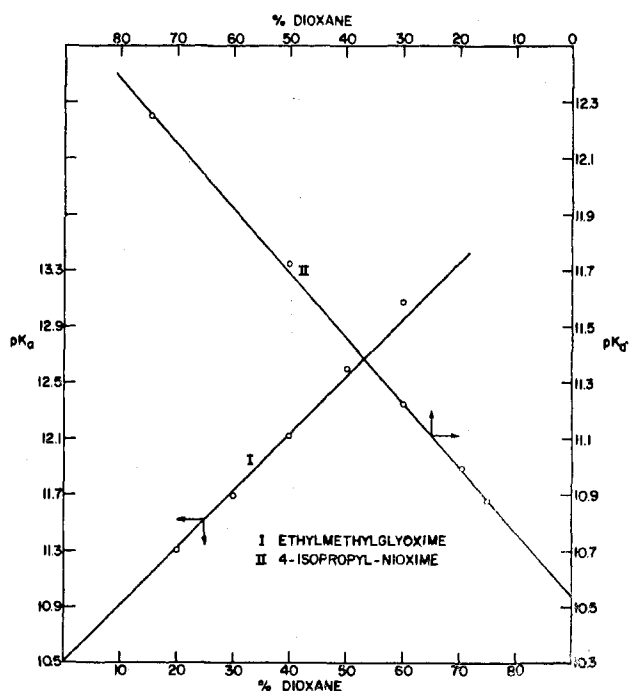


Fig. 2.—Acid dissociation constants of ethylmethylglyoxime and 4-isopropyl-nioxime as a function of dioxane concentration.

and in dioxane-water mixtures should serve as a good check on the applicability of eq. 1. These results are shown in Table II. The average value of the term, $(p\bar{K}_{a1} - pK_{a1})$, calculated from eq. 1 for 50% dioxane-water (v./v.) is 2.13, compared to the value of 2.07 which was determined experimentally. The average calculated value of the term for 75% dioxane-25% water (v./v.) is 2.83, compared to the value of 3.05 which was determined experimentally.

Because the various *vic*-dioximes included in this study are very similar, the assumption is made that eq. 1 also is applicable for other nickel(II)-*vic*-dioxime complexes.

TABLE I
ACID DISSOCIATION CONSTANTS OF SEVERAL *vic*-DIOXIMES AND THE STABILITY CONSTANTS OF THEIR NICKEL(II) COMPLEXES IN 75% DIOXANE-25% WATER MIXTURES^a

<i>vic</i> -Dioxime	$p\bar{K}_{a1}$	$\log \bar{K}_1$	$\log \bar{K}_2$
Dimethylglyoxime	13.53	10.96 ± 0.34	23.10 ± 0.14
Diethylglyoxime	13.93	$12.43 \pm .20$	$23.69 \pm .13$
Di- <i>n</i> -propylglyoxime	14.18	$13.14 \pm .35$	$23.86 \pm .65$
Ethylmethylglyoxime	13.55	$10.41 \pm .52$	$23.97 \pm .03$
4-Isopropyl-nioxime	12.27	$10.06 \pm .31$	$20.44 \pm .18$
Nioxime	13.11	$11.08 \pm .19$	$22.46 \pm .10$
4-Methyl-nioxime	13.07	$10.76 \pm .30$	$23.00 \pm .27$
3-Methyl-nioxime	13.23	$11.28 \pm .12$	$23.52 \pm .09$
Heptoxime	13.33	$12.26 \pm .19$	$24.68 \pm .23$

^a All constants were determined at 25° and at ionic strength 0.1.

TABLE II
STABILITY CONSTANTS OF COPPER(II) AND COBALT(II) DIMETHYLGLYOXIME COMPLEXES IN DIOXANE-WATER MIXTURES AND VALUES OF $(p\bar{K}_{a1} - pK_{a1})$

% dioxane	$\log K_1$	$1/2 \log K_2$	$(p\bar{K}_{a1} - pK_{a1})^a$	$(p\bar{K}_{a1} - pK_{a1})^b$
Copper(II)				
0	9.05	9.25
50	11.94 ^c	11.66 ^c	2.41	2.07
75	12.23	12.17	2.92	3.05
Cobalt(II)				
0	8.35	8.49
50	11.01	10.34	1.85	2.07
75	12.20	11.22	2.73	3.05

^a Calculated using eq. 1 and values of $1/2 \log K_2$. ^b Calculated from experimentally determined values of $p\bar{K}_{a1}$ and pK_{a1} . ^c Values taken from work of Charles and Freiser.¹⁸

TABLE III
ACID DISSOCIATION CONSTANTS OF *vic*-DIOXIMES AND STABILITY CONSTANTS OF NICKEL(II)-*vic*-DIOXIME COMPLEXES IN WATER SOLUTION

<i>vic</i> -Dioxime	$p\bar{K}_{a1}$	$(p\bar{K}_{a1} - pK_{a1})$	$\log k_1$	$\log k_2$	$\log K_2$	Ref.
Dimethylglyoxime	10.48	3.05	7.91	9.09	17.00	^a
	10.6					^b
	10.46				17.23	^c
	10.66					^d
	11.1					^e
Ethylmethylglyoxime	10.41	3.14	7.27	9.99	17.26	^a
Diethylglyoxime	10.67	3.26	8.97	8.20	17.17	^a
Di- <i>n</i> -propylglyoxime	10.81	3.27	8.77	8.35	17.12	^a
4-Isopropyl-nioxime	10.53	1.74	8.42	8.34	16.76	^a
Nioxime	10.55	2.56	8.52	8.82	17.34	^a
	10.6					^b
	10.4					^f
3-Methyl-nioxime	10.61	2.62	8.66	9.62	18.28	^a
4-Methyl-nioxime	10.54	2.53	8.27	9.71	17.94	^a
Heptoxime	10.71	2.62	9.62	9.81	19.44	^a
	10.7					^b

^a Values from this work. ^b C. V. Banks and A. B. Carlson, *Anal. Chim. Acta*, **7**, 291 (1952). ^c D. Dyrssen, F. Krasovec, and L. G. Sillén, *Acta Chem. Scand.*, **13**, 50 (1959). ^d V. M. Bochkova and V. M. Peshkova, *Zh. Neorgan. Khim.*, **3**, 1131 (1958). ^e A. K. Babko and P. B. Mikhelson, *Zh. Anal. Khim.*, **6**, 267 (1951). ^f P. E. Wenger, D. Monnier, and W. Bachmann-Chapuis, *Anal. Chim. Acta*, **15**, 473 (1956).

The stability constants in water were calculated from the stability constants in 75% dioxane-25% water (v./v.) and $(p\bar{K}_{a1} - pK_{a1})$. The results are given in Table III.

Solubility Product Constants.—Nickel perchlorate and the *vic*-

dioxime were mixed in stoichiometric amounts, shaken at a room temperature of 25° for 2 hr., and the pH was measured. Between 0.1000 and 1.00 ml. of 0.05874 *M* nickel solution was added with a micropipet to a solution of the *vic*-dioxime. The volume of the sample was adjusted by adding a known amount of water. The ionic strength was adjusted by using a solution of sodium perchlorate. The values of the activity coefficients are those reported by Kielland.²² The pH of the mixture was measured without filtering. The values for pK_{sp} are reported in Table IV.

Calculation of pK_s .—The intrinsic solubility constants for the nickel(II) complexes of dimethylglyoxime, nioxime, 4-isopropylnoxime, 3-methylnoxime, 4-methylnoxime, and heptoxime were calculated from the values of K_{sp} from this work, the work of Banks and Barnum,² and the calculated values of K_2 . These values for pK_s are reported in Table IV.

TABLE IV

VALUES OF THE INTRINSIC SOLUBILITY, NICKEL-NICKEL BOND LENGTH, SOLUBILITY PRODUCT, AND OVER-ALL STABILITY CONSTANT FOR THE NICKEL(II) COMPLEXES OF SEVERAL *vic*-DIOXIMES

<i>vic</i> -Dioxime	pK_s	Ni-Ni bond length in Å. ^a	pK_{sp}	$\log K_2$
Dimethylglyoxime	6.66	3.233	23.66	17.00
Ethylmethylglyoxime	5.70	^b	23.27	17.57
Diethylglyoxime	6.96	^c	24.21	17.17
Dipropylglyoxime	8.02	^c	25.14	17.12
4-Isopropylnoxime	11.08	3.19	27.84	16.76
Nioxime	11.06	3.237	28.39	17.34
4-Methylnoxime	10.32	3.24	28.25	17.94
3-Methylnoxime	9.34	3.47	27.62	18.28
Heptoxime	7.20	3.596	26.64	19.44

^a Values taken from work of Banks and Barnum.² ^b Does not form nickel-nickel bonds.⁶ ^c Crystal structure has not been determined.

Results and Discussion

Excluding Ni(DMG)₂ and nickel(II) 4-methylnoxime, there appears to be a smooth relationship between the intrinsic solubility constant and nickel-nickel bond distance in the crystals of the nickel(II) complexes of nioxime, 4-isopropylnoxime, 3-methylnoxime, and

(22) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

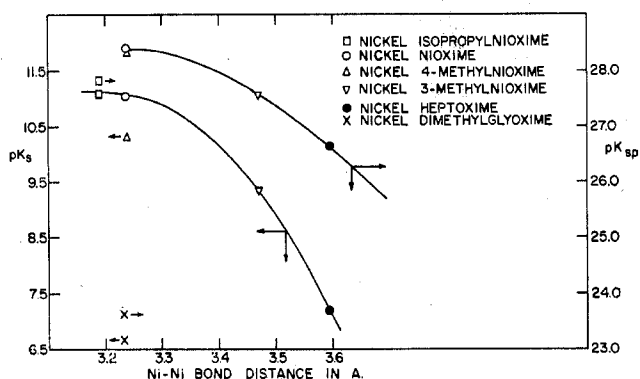


Fig. 3.—Dependence of pK_{sp} and pK_s on nickel-nickel bond distance in several nickel(II)-*vic*-dioxime complexes.

heptoxime (Table IV and Fig. 3). A similar relationship is shown for the solubility product constant and the nickel-nickel bond distance for the complexes. A long nickel-nickel bond distance results in a weak bond and less interaction between nickel atoms. Consequently, the intrinsic solubility constant of the complex would be expected to increase with increasing nickel-nickel bond distance.

The exceptionally low value of K_2 for nickel(II) 4-isopropylnoxime causes K_{sp} to be low and could explain why this complex does not correlate with the solubility product constant. The reason for the failure of nickel(II) 4-methylnoxime to exhibit a smooth relationship with the other alicyclic *vic*-dioxime complexes is not known.

Ni(DMG)₂ is much more soluble than the corresponding complexes for the alicyclic *vic*-dioximes studied. This may be due in part to the nature of the ligand. It may be that Ni(DMG)₂ is more soluble because of greater solvation of the complex. The complexes of nickel diethylglyoxime, Ni(DEG)₂, and nickel dipropylglyoxime, Ni(DPG)₂, are not included in Fig. 3 because their X-ray powder patterns indicate that they are not isostructural with Ni(DMG)₂.