mation of the ligand as a consequence of chelation, and the influence of different environments in complexes having different coördination numbers and/or containing different anions, may be considered responsible for the more complicated appearance of the ν(N–O) band of the complexes with respect to that of the free bipyO$_2$.

The two very strong absorptions appearing at 852 and 840 cm.$^{-1}$ in the spectrum of bipyO$_2$ are tentatively assigned to the NO bending vibrations.[4,5,23] In general, these two absorptions appear with similar intensity but slightly shifted to lower frequencies in the spectra of the metal complexes. Again, the presence of two NO bending bands indicates that the bipyO$_2$ molecule, both in the free solid and in the complexes, exists in the *gauche* conformation.

The Water Absorptions.—The spectra of the hydrated perchlorate complexes show a medium broad absorption at about 3600–3350 cm.$^{-1}$ (OH stretching) and absorptions of various intensities in the 1600 cm.$^{-1}$ region and below 500 cm.$^{-1}$, also assigned to the water of hydration.[12] Since the complex cations $[M(bipyO_2)_3]^{+n}$ are coördinatively saturated, the water of hydration is considered to be uncoördinated, in agreement with the observed values of the infrared absorptions. The hydrated compound $[Cu(bipyO_2)_2][PtCl_4]\cdot 4H_2O$ shows the OH stretching vibrations as a medium broad band between 3470 and 3250 cm.$^{-1}$. In the spectrum of the deuterated compound $[Cu(bipyO_2)_2][PtCl_4]\cdot 4D_2O$ this absorption is absent, whereas a new medium absorption (with splitting) assigned to OD stretching vibration appears at lower frequencies in the range 2625–2350 cm.$^{-1}$.

The spectrum of $[Cu(bipyO_2)_2][PtCl_4]\cdot 4H_2O$ shows two strong bands at 1671 and 1619 cm.$^{-1}$, and that of $[Cu(bipyO_2)_2][PtCl_4]\cdot 2H_2O$ shows two similar medium bands at 1628 and 1587 cm.$^{-1}$, whereas the anhydrous $[Cu(bipyO_2)_2][PtCl_4]$ as well as the deuterated $[Cu(bipyO_2)_2][PtCl_4]\cdot 4D_2O$ have no absorption in this range. In the CsBr region $[Cu(bipyO_2)_2][PtCl_4]\cdot 4H_2O$ has a broad, medium absorption in the range 667–612 cm.$^{-1}$, which becomes weak in the spectrum of $[Cu(bipyO_2)_2][PtCl_4]\cdot 2H_2O$, and in the spectra of the anhydrous $[Cu(bipyO_2)_2][PtCl_4]$ and of the deuterated $[Cu(bipyO_2)_2][PtCl_4]\cdot 4D_2O$ disappears, revealing one of the skeletal modes of the ligand at 637 cm.$^{-1}$. A water absorption in this region has been considered as arising from the rocking mode of coördinated water[24–26] and is consistent with the presence of the two strong bands at 1671 and 1619 cm.$^{-1}$ (OH$_2$ bending region) in the spectra of the hydrated copper(II) tetrachloroplatinate(II) complexes. The infrared evidence favors therefore the formulation of these compounds as salts of the cation $[Cu(bipyO_2)_2(H_2O)_2]^{2+}$. This formulation is compatible with the coördinative unsaturation of the bis-chelate cation $[Cu(bipyO_2)_2]^{2+}$ with respect to the tris-chelate cation $[Cu(bipyO_2)_3]^{2+}$ present in the perchlorate complex.

Acknowledgment.—This investigation was supported in part by the Public Health Service, Department of Health, Education, and Welfare, National Institutes of Health, and the U.S. Atomic Energy Commission.

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The Reaction of Nickel with Dioximes

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Received July 18, 1962

A series of symmetrically substituted *vicinal* dioximes was investigated with respect to hydrogen ion and Ni(II) ion. The pK_a values for eight dioximes were determined. Spectrophotometric data were obtained. Although 3:1 complexes of Ni(II) are well known, they are not well known when the ligand is a dioxime. Species with this stoichiometry are formed with dihydroxyglyoxime in ammoniacal solution and with dimethyl- and di-α-pyridylglyoximes in the presence of oxidizing agents. The NiR_3^- and the NiR_3^{-2} ions are proposed as the coördinated species existing in solution after the reaction of Ni(II) and dihydroxyglyoxime and Ni(II) and dimethyl- and dipyridylglyoximes under oxidizing conditions, respectively.

Introduction

In spite of the extensive work on nickel–dioxime systems, certain aspects of their chemistry have not been clearly defined. For example, in the presence of oxidizing agents, Ni(II) ion and dimethylglyoxime give a red solution[2] rather than a red precipitate. Considerable controversy still exists over the composition of the product. Various workers have reported that the nickel is oxidized to the trivalent,[3a] tetravalent,[2,3b] and even to the pentavalent state.[3b] It also has been

[1] An abstract of a thesis submitted by Mark A. Bambenek to the Graduate College of the State University of Iowa, 1961, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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proposed that the organic portion of the complex is oxidized and that the nickel remains in the divalent state.[3b] The stoichiometry of the complex has been reported as 2 : 1,[3a] 3 : 1,[3b] and 4 : 1.[4]

Present interest in the reaction of nickel with dioximes was concerned with the effect of the substituent on the central dioxime group and with the product formed, especially in the presence of oxidizing agents. Potentiometric, ion-exchange, and spectrophotometric studies were carried out on various Ni(II)–dioxime systems. Evidence is presented to support the formula NiR_3^{-2} for the soluble nickel–dimethylglyoxime complex formed in the presence of oxidizing agents. The NiR_3^- ion is proposed as the complex species produced by the reaction of Ni(II) and dihydroxyglyoxime.

Experimental

Reagents.—The dioximes used in this study were prepared by methods described in the literature. Compounds prepared can be represented as R–C(NOH)–C(NOH)–R, where R is C_6H_5,[5] C_4H_3O(furan)-,[6] Cl,[7] H,[8] C_5H_4N(α-pyridyl),[9] OH,[10] and NH_2.[11] The dioxime of 1,2-cyclohexanedione also was prepared (nioxime).[12] Dimethylglyoxime was obtained from the J. T. Baker Chemical Company. In general, the dioximes are prepared by the action of hydroxylamine on the corresponding carbonyl compound.

Nickel perchlorate hexahydrate was used as obtained from the G. Frederick Smith Chemical Company. Potassium persulfate was obtained from the Mallinckrodt Chemical Works.

Spectrophotometric Measurements.—All spectrophotometric measurements were made at 25° with a Cary Model 11 recording spectrophotometer. One-cm. matched silica cells were used for all measurements. Absorption spectra of the oximes and of the nickel complexes in aqueous solution were obtained with deionized water in the reference solution. Continuous variations and mole ratio studies were carried out on solutions prepared by mixing appropriate volumes of 1.0×10^{-4} *M* stock solutions of nickel(II) perchlorate and the reagent under consideration. For the nickel–dihydroxyglyoxime system, the final test solutions were made basic with 2 drops of 6 *M* ammonia. The dimethylglyoxime and dipyridylglyoxime systems were buffered at pH 9.0 and contained approximately 1.5 g. of potassium persulfate per 100 ml. of solution.

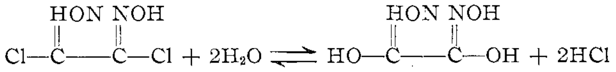
Potentiometric Measurements.—A Beckman Model G pH meter equipped with a general purpose glass electrode and a saturated calomel electrode was used for all pH measurements. The meter was standardized at 25° with commercially available buffer solutions. Solutions containing 1.0–3.0 mmoles of oxime and 1.5 mmoles of potassium hydroxide were titrated with standard hydrochloric acid. Potassium nitrate was added to all of the solutions to maintain an approximately constant value for the mean ion activity coefficient. Cyanuric acid ($pK_a = 6.53$) was titrated in a similar manner as a reference system.

Migration Studies.—A Hittorf type transference cell with platinum electrodes was used to investigate the influence of an electrical potential on the soluble complexes of nickel and substituted dioximes. A colored solution, 1.0×10^{-2} *M* in the nickel complex, 1 *M* in KNO_3, and 0.2 *M* in ammonia was placed in the center compartment with a 1 *M* solution of the salt and 0.2 *M* ammonia in the electrode compartments. The center compartment was isolated from the electrode compartments by medium porosity sintered glass disks to minimize transference by convection. An average current of 75 ma. was applied for 1 hr. The tris-1,10-phenanthroline-iron(II) complex was studied under identical conditions as a reference system. Migration of the colored nickel complex in a direction opposite to that of the ferroin complex indicated an anionic species.

Ion Exchange Studies.—An ion exchange reaction, with spectrophotometric measurement of the concentration of the nickel complex in solution, was used to determine the numerical charge on the nickel–dihydroxyglyoxime complex. A series of solutions containing 1.0×10^{-3} *M* nickel(II) ion, 4.0×10^{-3} *M* reagent, and varying concentrations of chloride ion ($1.0–2.0 \times 10^{-2}$ *M*) were prepared and measured spectrophotometrically at 330 mμ. An analytically weighed sample (approximately 0.4 g.) of dry Dowex 1–X8 anionic exchange resin in the chloride form was added to each solution. After equilibration at 25°, the absorbance of the supernatant solution was again measured at the above stated wave length. The data were treated in a manner similar to that outlined by Strickland.[13]

Results and Discussion

All of the dioximes studied, with the exception of the dichloro compound, are stable in solution for periods of 3 months or longer. Potentiometric and spectrophotometric measurements indicated that the dichloro compound is hydrolyzed immediately to form the dihydroxyglyoxime according to the reaction



$$Cl-\overset{HON}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}-Cl + 2H_2O \rightleftharpoons HO-\overset{HON}{\overset{\|}{C}}-\overset{NOH}{\overset{\|}{C}}-OH + 2HCl$$

Spectrophotometric data for the compounds in deionized water are presented in Table I. Addition of acid to solutions of the reagents has little effect on the absorption spectra except in the case of dipyridylglyoxime. A bathochromic shift of the absorption maximum from 230 to 236 mμ was observed when the pH of the solution was decreased from 6.73 to 3.15. With an increase in the pH, a bathochromic shift in the absorption maximum was observed for all reagents with a corresponding increase in absorbance in most cases. Thus, the anionic form of the dioxime absorbs at longer wave length with a higher absorptivity than does the neutral molecule.

TABLE I

DATA FOR DIOXIMES

Compound	λ_{max} (mμ)	ε	pK_a
Dihydroxyglyoxime	215	10,500	6.81 ± 0.02 8.66 ± 0.05
Diphenylglyoxime	237	16,000	8.50 ± 0.05
Glyoxime	240	18,000	8.88 ± 0.05
Difurylglyoxime	278	26,000	9.51 ± 0.02
Nioxime	240	2,400	10.10 ± 0.02
Dimethylglyoxime	226	13,000	10.14 ± 0.03
Diaminoglyoxime	235	10,500	. . .

Acid dissociation constants for the dioximes under consideration were calculated from potentiometric titration data. The pK_a values listed in Table I refer to the dissociation $RH \rightleftharpoons R^- + H^+$, where RH repre-

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sents the neutral oxime. The values represent a wide range of acidity with diamino- and dipyridylglyoximes being the least acidic followed by the familiar dimethylglyoxime. Since coördination of a dioxime with nickel usually involves the loss of a proton from the organic molecule, chelation reactions of reagents more acidic than dimethylglyoxime can be carried out in solutions which are less basic than those required for reactions with the dimethyl compound.

Dioximes containing basic functional groups, diamino- and dipyridylglyoximes, could not be titrated in aqueous solution in a manner similar to that for the above compounds. A pK_a of 11.38 was obtained for the diamino compound from a potentiometric titration in which the reagent was dissolved in acid and titrated with standard base. This value corresponds well with values obtained by Wenger, *et al.*,[14] by potentiometric and spectrophotometric measurements.

The same technique was employed for the dipyridyl compound. A pK_a of 2.48 for the monoprotonated species also was obtained.

Glyoxime and dipyridylglyoxime form soluble yellow colored species with nickel(II) ion which exhibit no absorption maxima in the near-ultraviolet. Dichloroglyoxime was found to give a soluble species with nickel which exhibits spectrophotometric characteristics, *i.e.*, wave length of maximum absorption and molar absorptivity, which are identical with those of the complex formed in the reaction of the metal ion with dihydroxyglyoxime.

An orange colored precipitate is formed with nickel and diaminoglyoxime in ammoniacal solution. This compound has been proposed as an analytical reagent for cobalt and nickel.[15]

The reaction of nickel(II) ion with dihydroxyglyoxime in ammoniacal solution resulted in the formation of a soluble yellow complex. This species exhibited a wave length of maximum absorption at 330 mμ with a molar absorptivity of 10,500 and appeared to follow Beer's law from 1–60 p.p.m. of nickel ion.

From continuous variations data (Table II), it is apparent that a complex with a 3:1 ratio of reagent to metal ion is formed, and ion migration studies showed that the complex was an anion.

TABLE II

CONTINUOUS VARIATIONS DATA

NICKEL(II)–DIHYDROXYGLYOXIME SYSTEM

Mole fraction Ni(II) ion	Absorbance 330 mμ	Absorbance 340 mμ
0.0	0.000	0.000
.1	.106	.064
.2	.208	.126
.3	.238	.150
.4	.206	.127
.5	.172	.106
.6	.125	.084
.7	.110	.064
.8	.064	.044
.9	.040	.024
1.0	.000	.000

TABLE III

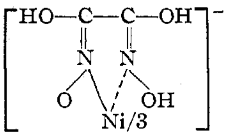
ION EXCHANGE STUDY OF NICKEL(II)–OHA SYSTEM

(0.3964 ± 0.020 g. of Dowex 1-X8)

Solution	C_{Cl^-}, M	$A_{s2}/A_{s1} - A_{s2}$
1	0.01	0.046
2	.02	.100
3	.03	.122
4	.04	.181
5	.05	.240
6	.06	.326
7	.07	.405
8	.08	.442
9	.09	.44
10	.10	.503
11	.15	.695
12	.20	1.021

The charge number was determined from data, presented in Table III, obtained on an equilibrium system consisting of chloride ion, the nickel complex, and an anionic exchange resin in the chloride form. Application of the treatment of Strickland[13] indicated a univalent species for the nickel(II) dihydroxyglyoxime complex.

Results of ion exchange, migration and spectrophotometric studies lead to the assignment shown below for the complex. This structure assumes an octahedral



configuration. While this configuration is not unknown in nickel(II) complexes, it has not been reported previously for a complex of nickel(II) with a dioxime. Complexes involving a 3:1 ratio of ligand to nickel(II) also are well known, but none involving a dioxime have been noted previously.

The effects of oxidizing agents on the complex formed between nickel(II) and dimethylglyoxime are shown in Table IV as the results of a mole ratio study. These data indicate that a 3:1 coördinated species is formed on reaction of ligand and metal ion in an oxidative medium, and ion migration studies showed that the species was an anion. Ion-exchange studies indicated that an ion of multiple charge was present. Exchange rates were too slow to make the studies con-

TABLE IV

MOLE RATIO STUDY OF NICKEL–DIMETHYLGLYOXIME SYSTEM

1×10^{-4} M Ni^{++}; 5×10^{-2} M $K_2S_2O_8$; pH 9.2 buffer

Dioxime ($M \times 10^4$)	Absorbance 460 mμ	Absorbance 475 mμ
0.00	0.00	0.00
1.00	.38	.26
2.00	.82	.60
3.00	1.25	.83
4.00	1.27	.86
4.50	1.28	.87
5.00	1.28	.87

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clusive. Thus it is possible that the nickel dimethylglyoxime species in an oxidative and basic medium exists as the divalent anion. This would confirm the conclusion reached by Šimek from magnetochemical studies.[16,17]

While the reaction of nickel and dipyridylglyoxime in basic solution produced no species of interest, a highly colored complex is formed in the presence of oxidizing agents. Wave lengths of maximum absorption at 405 and 455 $m\mu$ were found. The molar absorptivities at these wave lengths were 15,500 and 14,000, respectively. Molar ratio studies carried out on the system, as shown in Table V, indicated a reacting ratio of 3:1, while ion migration indicated an anionic species. Insofar as the system was investigated, it seems analogous to the Ni(II)–dimethylglyoxime reaction in the presence of oxidizing agents.

TABLE V

MOLE RATIO STUDY OF NICKEL–PYRIDYLGLYOXIME SYSTEM

1×10^{-4} M Ni^{++}; 5×10^{-2} M $K_2S_2O_8$; pH 9.2 buffer

Dioxime ($M \times 10^4$)	Absorbance 405 $m\mu$	495 $m\mu$
1.00	0.49	0.39
2.00	1.08	0.94
3.00	1.45	1.35
4.00	1.51	1.38
5.00	1.51	1.35

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The Preparation and Properties of Bis-(4-amino-3-pentene-2-ono)-nickel(II)

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Received September 4, 1962

Syntheses of bis-(4-amino-3-pentene-2-ono)-nickel(II) in both aqueous and non-aqueous media are described, as are some physical and chemical properties of this new red, diamagnetic nickel(II) chelate. Ultraviolet, visible, and infrared spectral data, solubilities, and reaction with water are discussed. A *trans*-configuration is apparent from the ligand field absorption bands of the spin-paired complex.

Introduction

Considerable interest has been generated in the stereochemistry of nickel(II) complexes with a stoichiometry of four coördinating groups per nickel ion inasmuch as three different structures are observed—planar, octahedral, and tetrahedral. Many of the paramagnetic nickel(II) complexes of this type, once thought to be tetrahedrally coördinated,[1] have been found to be octahedrally coördinated by polymerization. Structural studies include the trimeric anhydrous acetylacetonate,[2] nickel(II) chloride dihydrate,[3] $Ni(NCS)_2(thiourea)_2$,[4] and $Ni(NCS)_2(pyridine)_2$.[5] The same probably is true for the anhydrous nickel(II) salicylaldehyde complex.[6] Tetrahedral paramagnetic complexes of nickel(II) have been prepared through the use of large anions (Cl^-, Br^-, I^-, NO_3^-),[7] which prohibit the more favorable planar and octahedral configurations because of electrostatic repulsions. On the other hand, planar structures have been found for all the red, diamagnetic nickel complexes that have been studied by X-rays,[8] although large chelate rings can be used to distort the planarity.[9]

The β-diketone complexes of nickel have undergone considerable study and for 2,4-pentanedione an aqua, paramagnetic, octahedrally coördinated dihydrate,[10] as well as the green, paramagnetic, octahedral, anhydrous trimer[2] are known. Bulky 1,5-disubstitution on the β-diketone allows the isolation of red, diamagnetic complexes[11] which undoubtedly are planar, and in the case of bis-(2,6-dimethyl-3,5-heptanediono)-nickel(II) an equilibrium between the red, diamagnetic form and the green, paramagnetic form has been observed.[11]

It has been suggested by Holm[8] that the $Ni–O_2N_2$ type complexes represent an intermediate situation in bond strength in which the ligand field strength may or may not be sufficient to pair the electron spins. There is considerable data to support this view. It therefore seemed desirable to investigate the $Ni–O_2N_2$ complex most closely related to the nickel 2,4-pentanedione complexes and one which should have

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