haps the most likely to the authors. It is planned to search for additional cases where such second-order substitution rate terms may be observed to obtain information which may permit discrimination between these different possibilities.

Grinberg and Shagisultanova[8] reported that $PtBr_4^{2-}$ and either the *cis*- or *trans*-$Pt(NH_3)_2Br_2$ "traded" bromide ligands. They based this result on the fact that the exchange between these species occurred more rapidly than the exchange of bromide ion with $PtBr_4^{2-}$. It seems possible in view of the present work that the exchange in these cases actually occurred by a mutually catalyzed exchange of the ligands in each complex with free bromide ion. An attempt will be made to investigate this possibility.

The present work does emphasize that considerable care is needed in the preparation of platinum(II) compounds for kinetic studies, because the presence of one complex may catalyze the substitution reactions of another complex. In addition, it does provide a further indication that substitution reactions of platinum(II) compounds contain complications which have not been generally recognized previously.

Acknowledgment.—The authors wish to acknowledge the assistance of Jane Vanderkooi in some of the chemical and counting operations.

[8] A. A. Grinberg and G. A. Shagisultanova, *Radiokhimiya*, **2**, 592 (1960).

CONTRIBUTION FROM THE OLIN MATHIESON RESEARCH CENTER,
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Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. III. The Divalent Nickel Complex with 2,6-Bis(1,3-diiminoisoindolin-1-yl)pyridine

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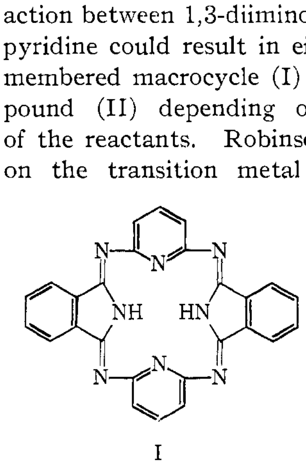
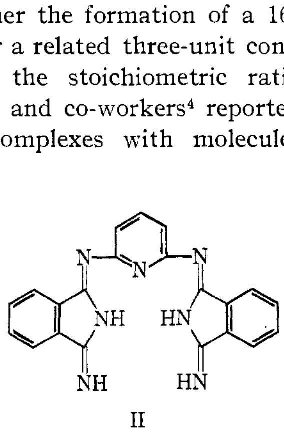
The divalent nickel ion coordinates with 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine in a bidentate fashion resulting in two types of complexes, $(NiLX_2)$ and $(NiL_2)X_2$, where X is a univalent anion. This ligand contains five nitrogen atoms which are potential sites for coordination: the two terminal imino groups, the two isoindoline ring atoms, and, finally, the pyridine ring nitrogen. By utilization of a series of ligand reactions, it has been concluded that the points of attachment are one of the isoindoline ring nitrogens and the pyridine nitrogen.

Introduction

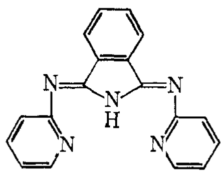
The formation of novel types of conjugated molecules by the condensation of 1,3-diiminoisoindoline with appropriate diimines was first described by Linstead and Elvidge.[1-3] They reported that the reaction between 1,3-diiminoisoindoline and 2,6-diaminopyridine could result in either the formation of a 16-membered macrocycle (I) or a related three-unit compound (II) depending on the stoichiometric ratio of the reactants. Robinson and co-workers[4] reported on the transition metal complexes with molecules similar to II. For example, 1,3-diiminobis(2-pyridyl)isoindoline (III) coordinates in a tridentate manner through the three ring nitrogens.



I



II



III

In this report, several varieties of divalent nickel complexes with II and some related molecules are described and characterized.

Experimental Section

Materials.—2,6-Diaminopyridine was obtained from the Aldrich Chemical Co. and purified before use. The other chemicals are standard inorganic reagents.

Synthesis.—**1,3-Diiminoisoindoline** was synthesized by the method of Elvidge and Linstead;[1] mp 194–196° (lit.[1] 194–195°).

2,6-Bis(1,3-diiminoisoindolin-1-yl)pyridine.—This compound was prepared by the method of Elvidge and Golden;[2] mp 241–243°.

[Dichloro-2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine]nickel-(II).—Nickel chloride hexahydrate (1.7 g, 0.0071 mole) was dissolved in butanol. To this, a butanol solution of 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine (2.6 g, 0.007 mole) was added rapidly, with stirring. A yellow crystalline material precipitated

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[1] J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5008 (1952).

[2] J. A. Elvidge and J. H. Golden, *ibid.*, 700 (1957).

[3] J. A. Elvidge and R. P. Linstead, *ibid.*, 5000 (1952).

[4] M. A. Robinson, S. I. Trotz, and T. J. Hurley, *Inorg. Chem.*, **6**, 392 (1967).

TABLE I

PROPERTIES OF THE COMPLEXES

		Magnetic data		Conductivity, mhos cm^{-1}		Spectral data, cm^{-1}	
Complex[a]	Color	$10^6\chi_m$	Moment, BM	DMF	CH_3NO_2	NH	NH_2
$Ni(DIP)Cl_2$	Yellow	5876	3.7	45	. . .	3200	
$Ni(DIP)_2(ClO_4)_2$	Brown	4014	3.1	133	160	3200 3350	. . .
$Ni(DIPO)_2$	Green	341	~0[b]	<1	. . .	. . .[c]	. . .
$Ni(DIPN)_2$	Blue	201	~0[b]	<1	. . .	. . .	3350 3450

[a] Abbreviations are defined in the body of the paper. [b] Small amounts of residual paramagnetism remain. [c] The NH absorption could not be unambiguously assigned.

TABLE II

SPECTRAL DATA IN THE 350–1500-mμ REGION

	In Nujol		In DMF		
Complex	Absorption, cm^{-1}	Assignment	Absorption, cm^{-1}	ϵ	Assignment
$Ni(DIP)Cl_2$	7,900	$^3T_1(F) \rightarrow {}^3A_2(F)$			
	14,000	$^3T_1(F) \rightarrow {}^3T_1(P)$			
	25,500				
$Ni(DIP)_2(ClO_4)_2$	12,700	$d_{xy} \rightarrow d_{x^2-y^2}$	13,300	126	d–d transition
			14,500	132	d–d transition
	21,300		21,300	25,000	
			23,300	34,000	
	25,500		25,000	42,000	
			25,900	40,000	
$Ni(DIPO)_2$	14,600	$d_{xy} \rightarrow d_{x^2-y^2}$			
	15,500	Charge transfer			
	29,000				
$Ni(DIPN)_2$	13,500	Charge transfer			

from solution. It was filtered, washed successively with methanol and ether, and dried *in vacuo* over P_4O_{10} at 100°; yield 85%. *Anal.* Calcd for $(C_{21}H_{15}N_7)NiCl_2$: C, 50.9; H, 3.0; N, 19.8; Cl, 14.3; Ni, 11.9. Found: C, 50.9; H, 3.3; N, 19.9; Cl, 14.7; Ni, 11.7.

Bis[2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine]nickel(II) Perchlorate.—A solution of nickel perchlorate hexahydrate (2.4 g, 0.10 mole) in butanol was added slowly, with stirring, to a butanol solution of 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine (8.0 g, 0.022 mole). The solution was refluxed for 15 min. The red-brown solid that precipitated was filtered, washed successively with methanol and ether, and dried *in vacuo* over P_4O_{10} at 100°; yield 75%. *Anal.* Calcd for $[(C_{21}H_{15}H_7)_2Ni](ClO_4)_2$: C, 51.0; H, 3.0; N, 19.8; Ni, 6.0. Found: C, 51.1; H, 3.2; N, 19.7; Ni, 5.8.

Bis{1-[2-(1,3-diiminoisoindolin-1-yl)pyrid-6-yl]-1-imino-3-oxoisoindolinato}nickel(II).—Into a 3-neck, 500-ml flask equipped with a condenser and a magnetic stirrer were placed 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine (5.1 g, 0.014 mole), nickel chloride hexahydrate (1.66 g, 0.007 mole), and 300 ml of 1,2,4-trichlorobenzene. The mixture was allowed to reflux for 20 hr during which time ammonium chloride was deposited in the condenser. It was necessary periodically to remove this solid so as to prevent clogging in the condenser. The blue-green solid that formed during the reaction period was filtered, washed successively with hot water, ethanol, and ether, and recrystallized from hot *o*-dichlorobenzene. It was dried *in vacuo* over P_4O_{10} at 210°; yield 40%. *Anal.* Calcd for $(C_{21}H_{13}N_6O)_2Ni$: C, 63.9; H, 3.3; N, 21.3; Ni; 7.5. Found: C, 63.2; H, 3.4; N, 21.2; Ni, 7.1.

An alternative procedure was adapted for the synthesis of this compound. [Dichloro-2,6-bis(1,3-diiminoisoindolin-1-yl)-pyridine]nickel(II) (4.95 g, 0.001 mole) was placed in 200 ml of 1,2,4-trichlorobenzene and the solution was held at reflux for 20 hr during which time it was noted that ammonium chloride formed in the condenser. The blue-green solid that formed was treated in a manner similar to that described in the previous method. The compounds prepared by the two methods were shown to be identical by comparison of the infrared spectra.

Bis[1-(2-aminopyrid-6-yl)-1-imino-3-oxoisoindolinato]nickel(II).—This complex was isolated from an acid hydrolysis reaction involving bis{1-[2-(1,3-diiminoisoindolin-1-yl)pyrid-6-yl]-1-imino-3-oxoisoindolinato}nickel(II). The latter complex (2.66 g, 0.0034 mole) was mixed with 50 ml of a 50% hydrochloric acid solution and refluxed for 15 min. The blue material that was isolated was washed successively with several portions of hot water and ethanol and then refluxed in ether for 30 min. It was then filtered, recrystallized from *o*-dichlorobenzene, and dried *in vacuo* over P_4O_{10} at 210°; yield 75%. *Anal.* Calcd for $(C_{13}H_9N_4O)_2Ni$: C, 58.6; H, 3.4; N, 21.0; Ni, 11.1. Found: C, 59.2; H, 3.4; N, 21.0; Ni, 10.9.

The hydrochloric acid solution was cooled in an ice bath and a quantity of white crystals formed. They were recovered and identified by infrared spectroscopy and mixture melting point (197°) as phthalic acid. The aforementioned liquid was evaporated leaving some tan solid which was purified by vacuum sublimation. This solid, also, proved to be phthalic acid. By carefully weighing the phthalic acid, it was concluded that 2 moles of the acid/mole of complex was collected.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities were obtained at room temperature by the Gouy method using ferrous ammonium sulfate hexahydrate and nickel chloride hexahydrate as standards. Magnetic moment values were obtained by use of the spin-only formula. Diamagnetic corrections were made for the ligands and anions so that the reported values (Table I) are the moments attributable to the metal ions.

Conductivity Measurements.—Molar conductances were obtained by employment of an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 0.500 cm^{-1}. The measurements were made at 25° employing 10^{-3} M solutions and a bridge frequency of 1000 cps (Table II).

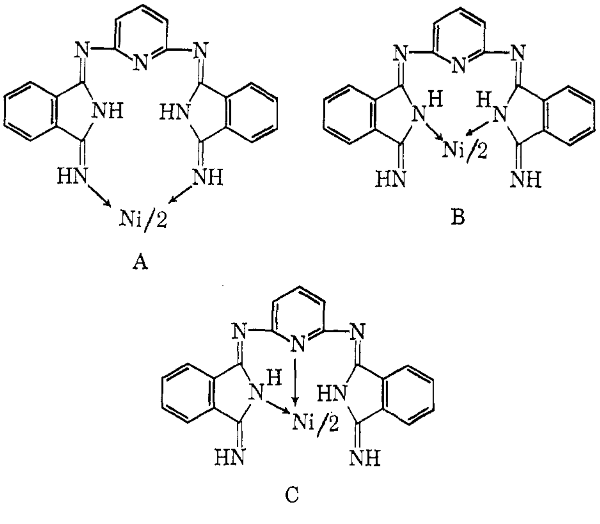
Spectra.—The spectra in the visible and near-infrared regions were obtained by employing a Cary Model 14 recording spectrophotometer and matched cells with fused-quartz windows. Results are listed in Table II.

All infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. Potassium bromide pellets were utilized and the results were checked out by employing mulls of Fluorolube and Nujol. Pertinent infrared spectral results are listed in Table I.

Results and Discussion

1,3-Diiminoisoindoline and 2,6-diaminopyridine condense in a 2:1 stoichiometric ratio to form 2,6-bis(1,3-diiminoisoindolin-1-yl)pyridine, hereafter abbreviated DIP. The subsequent reaction of this ligand with nickel chloride hexahydrate yields a highly crystalline, nonconducting, yellow solid of the general formula [Ni(DIP)Cl$_2$]. The magnetic moment of 3.7 BM and the spectral pattern in the 350–1500-mμ region (Table II) indicate that the ligand array surrounding the central metal ion is of tetrahedral symmetry. A further inference drawn from these data is that the organic ligand chelates in a bidentate manner. This was substantiated by additional experimentation to be discussed later. The reaction between DIP and nickel perchlorate hexahydrate results in the formation of the red-brown crystalline 2:1 complex.

As was just mentioned, DIP appears to coordinate in a bidentate manner. This is verified by a study of molecular models and is a result of the directional characteristics and spacing of the nitrogen atoms. There are three possible arrangements which will permit coordination involving two nitrogen atoms. They are depicted in IV. The first configuration, IVA, in which the two coordinating sites are the terminal imino nitrogens, is not likely to occur but should be considered; the second orientation, IVB, in which the two bonding nitrogen atoms are those associated with the isoindoline rings, and the final structure, IVC, which involves bonding through the pyridine nitrogen and one of the isoindoline ring nitrogen atoms, are both plausible arrangements. Since the isoindoline ring nitrogen is tetrahedrally oriented, these molecular configurations will not be planar. No other organization is sterically feasible.


A

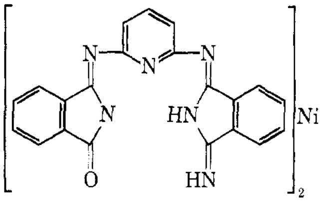
B

C

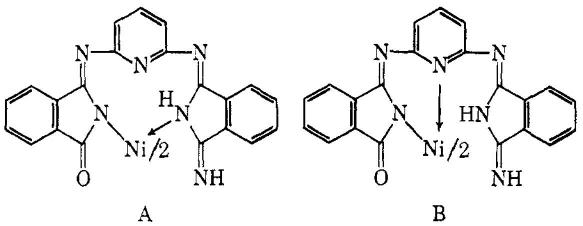
IV

In order to determine which of the three arrangements is the one that is operative, several reactions involving ligand transformations were carried out. At this point, it should be mentioned that the structural assignments are based on the preclusion of extensive ruptures and re-formations of ligand bonds. Of course, since nickel(II) forms kinetically labile complexes, the reader might choose not to ignore the possibility of bond reorganization. In this case, there would not be sufficient evidence to permit a definitive choice between the various structural possibilities, and the assignment must be regarded as tentative. The first reaction was concerned with the conversion of [Ni(DIP)Cl$_2$] into bis{1-[2-(1,3-diiminoisoindolin-1-yl)-pyrid-6-yl]-1-imino-3-oxoindolinato}nickel(II), V, hereafter abbreviated Ni(DIPO)$_2$. This was accomplished by refluxing the chloride complex in 1,2,4-trichlorobenzene, to which a small amount of water had been added. The over-all reaction may be written

$$2Ni(C_{21}H_{15}N_7)Cl_2 + 2H_2O \xrightarrow{C_6H_3Cl_3} Ni(C_{21}H_{13}N_6O)_2 + NiCl_2 + 2NH_4Cl$$


V

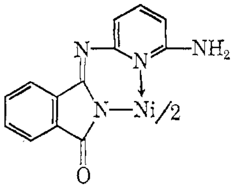
Alternatively, Ni(DIPO)$_2$ can be synthesized directly from nickel chloride hexahydrate and DIP in 1,2,4-trichlorobenzene. This complex has been characterized by elemental analyses, molar conductivity, magnetic susceptibility measurements (Table I), and visible spectroscopy (Table II). The results clearly indicate that the central nickel ion is surrounded by a square-planar array of ligand molecules. Further, one of the points of attachment must be through a covalent bond involving the nitrogen atom of the oxoisoindoline ring. Two configurations are possible, as depicted in VI. On the basis of these arrangements, the possibility of complexation occurring through the two terminal imino groups in the original [Ni(DIP)Cl$_2$] (IVA) is eliminated. To go from configuration IVA to either VIA or VIB would require the rupture of both imino–nickel bonds and the formation of two unrelated attachments, since it was pointed out previously that it is not sterically possible to have one of the terminal imino groups and another nitrogen atom bond simultaneously. Such a reorganization is to be questioned.


A

B

VI

The remaining problem is to choose between structures VIA and VIB. It is to be expected that, with the latter arrangement, it should be possible to remove the uncomplexed iminoisoindoline ring by hydrolysis, whereas, in the former, this should be excluded because both rings are coordinated to the nickel ion. Such is found to be the case. Hydrolysis with a 50% hydrochloric acid solution gives 2 moles of phthalic acid/mole of starting complex. The average per cent error for four hydrolyses runs was 11% based on theoretical recovery of phthalic acid. The resulting complex, bis[1-(2-aminopyrid-6-yl)-1-imino-3-oxoisoindolinato]nickel(II), abbreviated $Ni(DIPN)_2$, was isolated and characterized by elemental analyses, magnetic susceptibility measurements, molar conductance, and visible spectroscopy. The structure is depicted in VII. Because of the onset of a very strong charge-transfer band at very low energies, no assignment of d–d transitions could be made. Final corroboration for the structure is found in the infrared spectrum where the NH_2 stretching vibrations (although quite weak) occur at 3350 and 3450 cm^{-1}.



VII

On the basis of the previously described reactions, and minimizing the possibility of extensive ligand reorganization, it is concluded that the coordinating sites in [$Ni(DIP)Cl_2$] are the pyridine nitrogen and one of the isoindoline ring nitrogen atoms.

Acknowledgments.—The authors wish to thank Dr. John Babiec and the Microanalytical Group at Olin Mathieson for their invaluable assistance.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Deprotonation of Glycine and β-Alanine Complexes of Nickel(II)

BY GEORGE W. WATT AND JOHN F. KNIFTON

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Treatment of bis(glycinato)nickel(II) and bis(β-alaninato)nickel(II) with potassium amide in liquid ammonia at −33.5° has led to the isolation and characterization of the compounds $KNi(NHCH_2CO_2)(NH_2CH_2CO_2)$, $K_2Ni(NHCH_2CO_2)_2$, $KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)$, and $K_2Ni(NHCH_2CH_2CO_2)_2$. Both cases correspond to the successive removal of protons from the ligand nitrogen atoms; the doubly deprotonated species represent the maximum number of protons that may be abstracted under these conditions. The infrared spectra of these and the parent complexes have been studied to examine the effect of proton abstraction upon the nature of the metal–ligand bonds.

Earlier work has established that protons associated with the ligand nitrogen atoms in ethylenediamine[1–8] and diethylenetriamine[9,10] complexes are sufficiently acidic to permit their successive removal in appreciably basic media. An extension of these studies has since shown that proton abstraction from a coordinated amino group can be achieved with a number of other bidentate ligands. Here we report results from studies of the deprotonation of glycine and β-alanine complexes of nickel(II); this work was of particular interest since evidence for the successful deprotonation of the amino group coordinated to a 3d series transition metal has not been demonstrated previously.

Experimental Section

Methods.—Reactions in liquid ammonia and procedures for handling the products thereof were the same as described elsewhere.[11] The air-sensitive products were stored and/or transferred in a drybox containing a helium atmosphere maintained oxygen- and water-free by continuous exposure to liquid Na–K alloy.

Infrared spectra (Table I) were recorded with Beckman IR-7 and IR-11 instruments. Spectra in the region 600–3800 cm^{-1} were taken as mulls in Nujol and hexachlorobutadiene on NaCl plates. Spectra in the 200–700-cm^{-1} region were recorded using Nujol mulls on CsI plates. Typical spectra are shown in Figure 1.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kv and 15 ma. Exposure times were 12–18 hr; relative intensities were estimated visually. The *d* spacings corresponding to the most intense lines (with relative intensities in parentheses) are listed immediately following analytical data.

Nickel was determined gravimetrically as the dimethylglyoximate.[12] Carbon, hydrogen, and nitrogen analyses were performed, either in these laboratories using a Coleman Model 33 carbon–hydrogen analyzer and a Coleman Model 29 nitrogen analyzer or by commercial analytical laboratories.

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