the formation of a dative bond between the isoindoline ring nitrogen and the nickel ion. This results in a relatively strain-free six-membered isoindolenine ring in which the terminal imino nitrogen comes into close proximity to the ring carbon atom of the other coordinating ligand, to which the alkoxy group is bonded. Consequently, ring closure should be effected in a facile manner. This is found to be the case. Heating Ni($C_{21}H_{19}N_4O$)$_2$ (I-D) results in the splitting off of the alkoxy groups and the rearrangement of bonds involving ring closure resulting in the formation of nickel phthalocyanine. The other products, identified by mass spectrometry, are 1-pentanol and 1-pentanal.

Acknowledgment.—We wish to thank Mr. D. Vickers for ably assisting us in obtaining and interpreting the nuclear magnetic resonance spectra. In addition, we acknowledge the microanalytical group at Olin Mathieson for the expert handling of the samples reported herein.

Notes

Contribution from the Olin Mathieson
Research Center, New Haven, Connecticut

Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. I. Deprotonation of 1,3-Bis(2-Pyridylimino)isoindoline Complexes

By Martin A. Robinson, Samuel I. Trotz,
and Thomas J. Hurley

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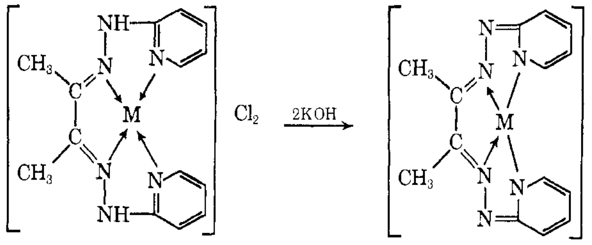
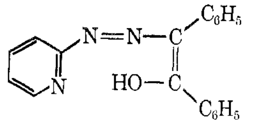
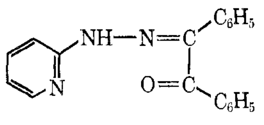
In 1958, Lions and Martin[1] first reported on the phenomenon of deprotonation of cationic complexes. In this unique and isolated incident, a diamagnetic complex was isolated from the reaction between cobalt(II) bromide and 2-pyridinal (2-pyridyl)hydrazone. The spin multiciplicity of the complex arose as a result of the oxidation of the cobalt(II) ion to the trivalent state accompanied by the reduction of one of the ligand molecules through the loss of a proton. Other experimenters[2-4] have shown that the deprotonation process is quite general and need not necessarily be associated with an oxidation–reduction reaction. In most cases, deprotonation can be brought about by treatment of the cationic complex with alkali, resulting in the formation of the neutral species with no alteration in the number of coordinating sites on the ligand molecule due to deprotonation. For example, the nickel chloride complex of butane-2,3-dione bis(2′-pyridylhydrazone) (I) is doubly deprotonated by the action of potassium hydroxide to yield the neutral complex (II).[5] There are some instances, however, where the number of coordinating positions have been altered by deprotonation.[2] Thus, in neutral solutions benzilmono(2-pyridyl)hydrazone acts as a tridentate chelating agent (III), whereas, in acid solution where the deprotonation can be prevented, the molecule appears then to function only as a bidentate ligand (IV).



I II



III



IV

In the work reported herein, deprotonation, in addition to being induced in the usual manner, can also be facilitated by altering the anionic component of the transition metal salt.

Experimental Section

Syntheses. 1,3-Bis(2-pyridylimino)isoindoline.—A solution of 2-aminopyridine (37.6 g, 0.4 mole) in hot butanol was added quickly to a butanol solution of 1,3-diiminoisoindoline (29.0 g, 0.2 mole). The solution was held at reflux for 4 hr and then cooled to room temperature. A yellow solid formed. It was filtered, washed with ether, recrystallized from methanol, and dried under vacuum at 60° for 8 hr; mp 189–192°. *Anal.* Calcd for $C_{18}H_{13}N_5$: C, 72.2; H, 4.4; N, 23.4. Found: C, 72.3; H, 4.4; N, 23.5.

Metal Perchlorate Complexes of 1,3-Bis(2-pyridylimino)isoindoline.—These complexes were synthesized by allowing a methanol solution of the metal perchlorate to react with a methanol solution of the ligand in a 1:2 stoichiometric ratio. The complexes formed immediately and were filtered, washed with methanol and ether, and dried under vacuum at 60°.

Preparation of Complexes from the Metal Chloride Salts.—These complexes were prepared from methanol in a manner analogous to that previously described for the perchlorate complexes but were recrystallized from nitrobenzene.

Preparation of Complexes from the Metal Acetate Salts.—These complexes were isolated out of methanol and recrystallized from nitrobenzene. Alternatively, formamide may be employed as the solvent. If the ratio of reactants is 1:1, a large amount of the bis complex still precipitates out, but evaporation of the solvent results in the isolation of a complex whose stoichiometry

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(1) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3855 (1958).
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TABLE I

CHEMICAL AND PHYSICAL DATA FOR THE COMPLEXES

			Analytical data, %								Magnetic data		
			Theory				Reported						
No.[a]	Complex	Color	C	H	N	Metal	C	H	N	Metal	$10^6\chi_M$ (cor)	Magnetic moment, BM	Infrared N-H str, cm^{-1}
1	$Fe(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot H_2O$	Green	49.6	3.2	16.1	6.4	49.6	3.4	15.7	6.1	12380	5.42	3330
2	$Co(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot 0.5H_2O$	Orange	49.9	3.1	16.2	6.8	50.1	3.4	16.2	7.2	9734	4.80	3320
3	$Ni(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot H_2O$	Gold	49.4	3.2	16.0	6.8	49.5	3.5	15.7	6.6	3840	3.01	3330
4	$Zn(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot H_2O$	Yellow	49.1	3.2	15.9	7.4	49.1	3.5	15.6	7.6	...	...	3330
5	$Cd(C_{18}H_{13}N_5)_2(ClO_4)_2$	Yellow	47.5	2.9	15.4	12.3	47.7	2.6	15.7	12.6	...	...	3330
6	$Fe(C_{18}H_{12}N_5)_2$	Gray	66.3	3.7	21.5	8.1	65.8	3.6	22.0	9.0	13347	5.66	...
7	$Co(C_{18}H_{12}N_5)_2$	Red	65.9	3.4	21.4	9.0	65.9	3.6	21.2	9.3	8812	4.59	...
7A	$Co(C_{18}H_{12}N_5)_2$	Red	65.9	3.4	21.4	9.0	65.6	3.7	21.2	9.4	11168	5.15	...
7C	$Co(C_{18}H_{12}N_5)_2\cdot 0.5H_2O$	Brown	65.1	3.8	21.1	8.9	64.9	3.7	21.4	9.4	9799	4.82	...
8	$Ni(C_{18}H_{12}N_5)_2$	Brown	65.9	3.4	21.4	9.0	65.7	3.3	21.5	9.0	4040	3.10	...
8A	$Ni(C_{18}H_{12}N_5)_2$	Brown	65.9	3.4	21.4	9.0	66.1	3.7	21.7	8.6	3871	3.04	...
8C	$Ni(C_{18}H_{12}N_5)_2$	Brown	65.9	3.4	21.4	9.0	65.9	3.7	21.3	8.9	3977	3.07	...
9	$Zn(C_{18}H_{12}N_5)_2$	Yellow	65.4	3.7	20.9	9.8	65.8	3.7	20.8	10.2	...	...	...
9C	$Zn(C_{18}H_{12}N_5)_2\cdot H_2O$	Yellow	63.6	3.8	20.6	9.6	63.5	4.0	21.0	9.0	...	...	...
10	$Cd(C_{18}H_{12}N_5)_2$	Yellow	61.0	3.4	19.8	15.8	61.1	3.4	19.7	16.2	...	...	...
11	$Ni(C_{18}H_{12}N_5)(C_2H_3O_2)$	Tan	57.7	3.6	16.8	14.2	57.4	3.3	16.7	14.8	3766	3.01	...

[a] Deprotonated samples, no. 6–10, were made from the perchlorate salt by treatment with potassium hydroxide; no. 7A and 8A were synthesized from the acetate salt; no. 7C, 8C, and 9C were obtained from the chloride salts. [b] N–H stretch for the free ligand falls at 3220 cm^{-1}.

indicates that one deprotonated ligand and one acetate group are coordinated.

Deprotonation of the Perchlorate Complexes.—In this procedure, the metal perchlorate complex was dissolved in methanol, and a twofold excess of potassium hydroxide, dissolved in methanol, was added rapidly. The deprotonated complex which precipitated from solution was filtered, washed with methanol, recrystallized from nitrobenzene, and dried under vacuum at 100°. The analytical results for all the complexes reported herein are listed in Table I.

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

Conductivity Measurements.—Molar conductances were obtained through the use 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 of dimethylformamide and a bridge frequency of 1000 cps. The protonated complexes gave molar conductance values between 129 and 139 ohm^{-1} cm, which are typical of di-univalent electrolytes. The deprotonated complexes were all nonconductive ($\lambda_M < 1.0$ ohm^{-1} cm).

Spectra.—The spectra in the visible and far-infrared regions were obtained by employing a Cary Model 14 recording spectrophotometer and matched cells with fused-quartz windows. Measurements were made in dimethylformamide and Nujol (Table II). The infrared scans were made on 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 (Table I).

Discussion

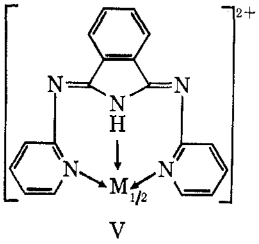
The reaction between 1,3-bis(2-pyridylimino)isoindoline and divalent metal perchlorates results in characteristic octahedral complexes of the general formula $(ML_2)(ClO_4)_2$ (V) in which the ligand chelates in a tridentate manner through the amino and two heterocyclic imino nitrogen atoms. The acidic nature of the amino proton affords an opportunity to transform these cationic complexes into the uncharged species by deprotonation. This is accomplished in a facile manner by the action of potassium hydroxide with the subsequent formation of the stable neutral species of the general formula $M(L\text{-}H_2)$ (VI). The stability of these neutral complexes may be a result of the various canoni-

TABLE II

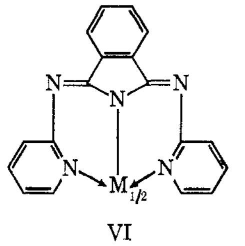
SPECTRAL DATA FOR THE COMPLEXES

Complex	Solvent	Absorption, cm^{-1}	Extinction coeff
$Ni(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot H_2O$	Nujol[a]	11,013 sh	...
		11,678 wide	...
		23,256 sh	...
		26,677 sh	...
		42,017	...
$Ni(C_{18}H_{13}N_5)_2(ClO_4)_2\cdot H_2O$	DMF	11,490	17
		14,493	8
$Ni(C_{18}H_{12}N_5)_2$	Nujol	11,428 very wide	...
		21,053	...
		22,528	...
		30,166	...
		43,478	...
$Ni(C_{18}H_{12}N_5)_2$	DMF	10,930	11
		11,494	12
		15,267	14
$Ni(C_{18}H_{12}N_5)(C_2H_3O_2)$	Nujol	12,438	...
		13,569 sh	...
	DMF	11,494	19
		15,151 sh	...

[a] The solid was mulled in Nujol and run as a paste.

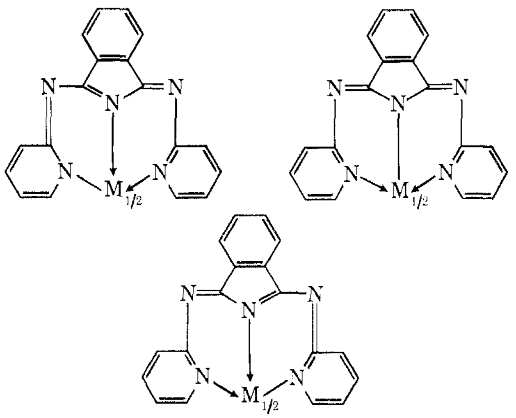


V



VI

cal forms that can be written for the deprotonated analog (VII).



VII

More interesting, perhaps, is that deprotonation can be brought about by altering the anion associated with the transition metal salt. In contrast to the perchlorate salt which gives rise to the protonated complex (V), the transition metal chloride or acetate derivative in conjunction with two ligand molecules yields the deprotonated species (VI) directly. A possible explanation for this phenomenon is the extreme acidity of the amino proton which requires the presence of the least basic anion for its retention. In the case of the copper(II) system, spontaneous deprotonation occurs even in the presence of the perchlorate ions. Thus, the reaction of copper(II) perchlorate with 1,3-bis(2-pyridylimino)isoindoline does not result in the precipitation of the protonated cationic species as was the case with the other metal analogs. Rather, in about 2 days, a green, crystalline solid forms which is the deprotonated complex.

The transformation of the cationic complexes into their neutral counterparts is accompanied by alterations in both chemical and physical properties. Changes in color, increased solubility in organic solvents, transformation to nonconductors, and the disappearance of the infrared absorption arising from the N–H stretch accompany the formation of the neutral species. In contrast is the consistency exhibited by the magnetic moments of the divalent iron, cobalt, and nickel complexes which indicate that the octahedral array is retained after deprotonation. This is further confirmed by spectral studies on the nickel(II) derivatives in the visible and near-infrared regions in which it is noted that the absorptions remain nearly constant in both position and intensity (Table II). Unfortunately, in the spectra obtained from DMF solutions, no d–d transitions could be observed below 650 mμ owing to the onset of strong charge-transfer bands.

The reaction of nickel acetate with 1,3-bis(2-pyridylimino)isoindoline in a 1:1 molar ratio results in the separation of a small amount of a complex of the general formula $M(L-H)(C_2H_3O_2)$. The nonconducting nature of this complex indicates that the acetate anion is coordinated to the nickel. The magnetic moment of 3.01 BM and the positions of absorptions in the visible and near-infrared regions make it difficult to assess the structure of this complex in a definitive manner. However, a five-coordinate molecule, in which the acetate anion is bonding in a bidentate fashion, is a possibility. A transformation to an octahedral arrangement, probably through the coordination of solvent molecules, is noted when the complex is dissolved in dimethylformamide. We are still in the process of assessing this structure.

Acknowledgment.—The authors wish to thank the microanalytical section at Olin Mathieson for their adept handling of the samples reported herein.

Contribution from the
Olin Mathieson Chemical Corporation,
Chemicals Division, New Haven, Connecticut

Aminophenoxy- and Isocyanatophenoxyphosphonitriles

By Gerhard Ottmann, Henry Lederle,
Haywood Hooks, Jr., and Ehrenfried Kober

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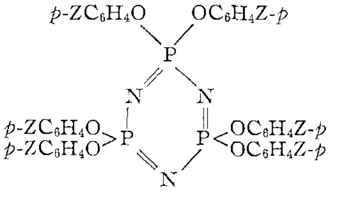
By virtue of their structural relationship to thermally stable trimeric and tetrameric aryloxy substituted phosphonitriles[1,2] and to polymers obtained by condensation of cyclic phosphonitrilic chlorides with polyfunctional aromatic compounds,[3,4] aminophenoxy- and isocyanatophenoxy-substituted cyclic phosphonitriles are attractive intermediates for the formation of thermally stable, fire-resistant fluids and polymers. Since reactions of cyclic phosphonitrilic chlorides with bifunctional compounds such as *p*-aminophenol or hydroquinone[4] lead inevitably to the formation of highly cross-linked polymers, other routes for the preparation of polyfunctional aminophenoxy- and isocyanatophenoxyphosphonitriles had to be found.



I, Z = NO_2
II, Z = NH_2
III, Z = NCO
IV, Z = $NHCOOCH_3$
V, Z = $NHCOOC_4H_9$

The accessibility of 2,2,4,4,6,6-hexakis(*p*-nitrophenoxy)-phosphonitrile (I) in high yield by a recently reported procedure[5] encouraged us to attempt the synthesis of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) by hydrogenation of I. Although the PN nucleus of cyclic phosphonitrilic chloride does not survive hydro-

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(1) E. Kober, H. Lederle, and G. Ottmann, *ASLE Trans.*, **7**, 389 (1964).

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