

cooling caused deposition of the crude product (salts 1, 2a). (B) This was similar to A except that a salt other than a perchlorate was used (salts 2b, 2c, 2d, and 2e). (C) This also was similar to A but the metal salt used was K_2PdCl_4 .

Preparation of Neutral Complexes.—(D) An aqueous solution of the metal salt (1 molar proportion) was treated with slightly more than the theoretical amount of ammonium hydroxide solution to form the water-soluble complex ammine salt. This solution was then added to a solution of the ligand I (2 molar proportions) in ethanol. The neutral complex III separated after evaporation and cooling (neutral complexes 5, 6, and 7). (E) A

solution of the complex salt II (prepared by A, B, or C) in ethanol-water was treated with 5 *N* sodium hydroxide solution in slight excess, and the neutral complex was extracted into benzene, washed with water, dried with anhydrous sodium sulfate, and the solvent removed (neutral complexes 5, 6, and 7).

Acknowledgments.—The authors gratefully acknowledge the assistance of the Petroleum Research Fund of the American Chemical Society which made this work possible and the help of Miss B. Stevenson for the organic microanalyses recorded.

CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY,
THE UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

Tridentate Chelate Compounds. IV. Metal Complexes from α -Diketone Mono- α -pyridylhydrazone Type Ligands

BY BARRY CHISWELL,¹ FRANCIS LIONS, AND MURIEL L. TOMLINSON²

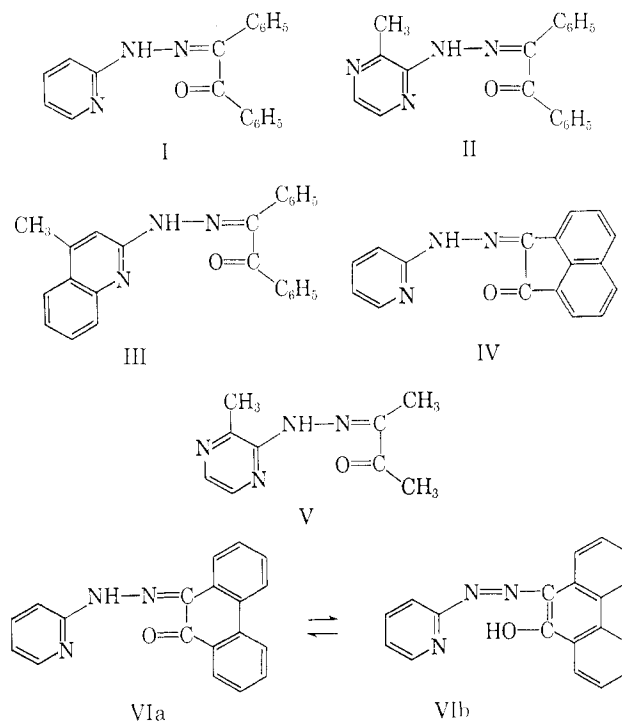
Received August 23, 1963

Several α -diketones, such as benzil, acenaphthenequinone, and phenanthraquinone, have been condensed with *N*-heterocyclic hydrazines of the amidrazone type, such as 2-pyridylhydrazine, to form monohydrazones. In neutral alcoholic solution these hydrazones react with salts of certain transition metals as tridentate chelating agents with loss of the imino hydrogen atom. In acid solutions the deprotonation can be prevented and the ligands appear then to function only as bidentate chelating agents. Studies are reported most fully for copper(II) and nickel(II) salts. A red organic-solvent-soluble six-coordinate sodium complex is also reported. The structures of all these complexes have been deduced after consideration of infrared, ultraviolet, and visible spectra, conductivity measurements, and magnetic studies.

It is well known that whereas certain types of α -dicarbonyl compounds—and, as precursors of such compounds, α -ketols—readily yield osazones when caused to react with substituted hydrazines, such as phenylhydrazine, some α -diketones are extremely reluctant to form osazones. In these instances reaction usually stops at the monophenylhydrazone stage. We have found that benzil, phenanthraquinone, and acenaphthenequinone react with 2-pyridylhydrazine to give the mono-(2-pyridylhydrazone) only. There was no evidence of osazone formation, and we have been unable to prepare bis-(2-pyridylhydrazones) by any method³ from these ketones. Similar behavior was observed when 4-methyl-2-quinolyldiazine was caused to react with benzil or when 3-methyl-2-pyrazinylhydrazine was caused to react with benzil. A monohydrazone was prepared also from this latter hydrazine and biacetyl. However, it was also possible to obtain the osazone from these two reactants under forcing conditions.

The six mono-(2-azaaryl)hydrazones I–VI (Table I) are all capable of functioning as tridentate chelating agents. The typical red “azo” color of VI when contrasted with the yellow to orange colors of the other hydrazones suggests that it should be formulated as a 2-pyridineazophenol (VIb) and that its properties could well resemble those of the well-known 1-(2'-

pyridineazo)-2-naphthol and 4-(2'-pyridineazo)resorcinol. The interrelationships of the quinonehydrazone



and azophenol forms in such compounds as VI have often been studied.⁴

(1) Petroleum Research Fund Fellow, University of Sydney.

(2) Visiting Petroleum Research Fund Fellow at University of Sydney from University of Oxford.

(3) Cf., e.g., H. Ingle and H. H. Mann, *J. Chem. Soc.*, 67, 611 (1895).

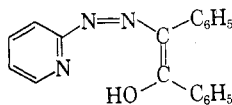
(4) For an account, see, e.g., H. Zollinger "Diazo- and Azochemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 322–327.

TABLE I
LIGANDS^a

Compd. no.	Name	Formula	M.p., °C.	Color	Analyses, %			
					C	H	N	
I	Benzil mono-(2-pyridyl)-hydrazone	C ₁₉ H ₁₅ N ₃ O	140	Colorless	Calcd.	75.8	5.0	14.0
					Found	75.6	5.1	14.3
II	Benzil mono-(3-methyl-2-pyrazinyl)hydrazone	C ₁₉ H ₁₅ N ₄ O	178	Deep yellow	Calcd.	72.2	5.1	17.7
					Found	72.0	4.9	17.8
III	Benzil mono-(4-methyl-2-quinolyl)hydrazone	C ₂₄ H ₁₉ N ₃ O	166	Yellow	Calcd.	78.8	5.2	11.8
					Found	78.7	5.3	11.8
IV	Acenaphthenequinonemono-(2-pyridyl)hydrazone	C ₁₇ H ₁₁ N ₃ O	182	Orange	Calcd.	74.6	4.0	15.4
					Found	74.0	4.0	15.4
V	Biacetylmono-(3-methyl-2-pyrazinyl)hydrazone	C ₉ H ₁₂ N ₄ O	169	Deep yellow	Calcd.	56.2	6.2	29.2
					Found	56.0	6.3	29.3
VI	Phenanthraquinone mono-(2-pyridyl)hydrazone	C ₁₉ H ₁₃ N ₃ O	190	Red	Calcd.	76.3	4.3	14.0
					Found	76.3	4.6	13.3

^a Solvent of recrystallization for I-V was ethanol; for VI it was benzene.

That the five substances I-V might be regarded as possessing (as limiting structures) azo-enol structures (e.g., Ia instead of I) at once suggests the possibility of their molecules being able to function, after deproton-



Ia

ation, as tridentate chelating groups, similarly to the deprotonated residues of 1-(2'-pyridineazo)-2-naphthol and 4-(2'-pyridineazo)resorcinol.

We now report that each of these six substances I-VI can function as a tridentate chelating agent. After coordination with salts of certain transition metals and deprotonation they yield highly colored neutral complexes which are distinguished by their high solubility in organic solvents. We have found also that they can coordinate without deprotonation but then only, apparently, as bidentate chelating agents. Some aspects of this coordination chemistry are now discussed. For simplicity in formulation any one of the ligands I-VI is referred to generally as HLig. If the ligand molecule during coordination is deprotonated the H is dropped. Where a specific ligand is referred to its number is included. Thus, for example [Cu(LigI)Cl] denotes the neutral complex obtained by coordination as a tridentate ligand of one deprotonated benzil mono-(2-pyridyl)hydrazone residue and one chlorine ion with a copper(II) ion.

Experimental

Most of the experimental results obtained are tabulated. The following brief notes are necessary.

Solvents.—References to the solvents used for recrystallization are by letters according to the code: water, W; ethanol, A; benzene, B; chloroform, C. When a substance was not recrystallized it is marked N.r.

Conductivities were measured with a Philips Philoscope in which platinum-coated electrodes of the dip type were used. Unless otherwise noted the values quoted are given in reciprocal ohms for 10⁻³ M solutions in nitrobenzene of analytical reagent quality at 25.0 ± 0.1°. The letters N.E. (nonelectrolyte) indicate that the value of Λ_{1000} found for the compound was less than 0.1 reciprocal ohm.

Magnetic moments were measured on a Gouy balance at room temperature.

Ligands.—The general method of preparation used was to dissolve the α -diketone in ethanol, add slightly more than one molecular proportion of the hydrazine and a little glacial acetic acid, and then heat under reflux for 15 min. Cooling in an ice bath then usually caused the monohydrazone to crystallize. The yields varied between 65 and 80% (Tables I and Ia).

TABLE Ia
INFRARED DATA FOR LIGANDS, CM.⁻¹

Ligand	—CCl ₄ —		Nujol C=O
	N—H	C=O	
I	3317	1652	1632
II	3340	1650	
III	3311	1653	1632
IV	3250	1674	1645
V	3350	1685	1642
VI ^a			

^a Exhibits an OH band at 3579 cm.⁻¹.

Preparation of Complexes.—The variant methods employed are given below.

(1) The ligand (2 molecular proportions) in ethanol solution was treated with a solution of the metal perchlorate (1 molecular proportion) in water. Evaporation followed by cooling then yielded the crude product.

(2) Similar to 1 but using the metal halide.

(3) Similar to 1 but using a salt containing the [PdCl₄]⁻² or [AuCl₄]⁻ ion instead of the metal perchlorate.

(4) A solution of the ligand (2 moles) in ethanol was treated with a solution of the metal perchlorate (1 mole) in water and the intensely colored substance produced extracted into benzene or chloroform. This extract was washed, then dried with anhydrous sodium sulfate, and the solvent was then removed, leaving the crude product.

(5) Similar to 4 but using 3 molecular proportions of ligand to one of metal perchlorate.

(6) A solution of the ligand (2 moles) in ethanol was made acid with 10 N hydrochloric acid. Then a solution of the copper(II) halide (1 mole) in ethanol was added. Evaporation, then cooling, led to separation of the product.

(7) A solution of the ligand (2 moles) in ethanol was treated with 5 N sodium hydroxide solution (ca. 1.5 moles). The red solution then was extracted with benzene. From the benzene extracts the bright red sodium complex was recovered by evaporation and cooling.

Anal. Calcd. for C₃₈H₃₁N₆NaO₃: C, 71.0; H, 4.8; N, 13.1; Na, 3.6. Found: C, 69.8; H, 4.9; N, 13.0; Na, 3.4. The residue remaining after C and H determination was sodium carbonate. Weighing of this residue gave the sodium figure and a correction figure for the carbon estimation of 0.9%, thus bringing the found C to 70.7%.

TABLE II
COPPER(II) COMPLEXES^a

Compd. no.	Ligand	Formula	M.p., °C.	Magnetic moment, B.M.	Infrared bands, cm. ⁻¹		Analyses, %					
					NH	C=O	C	H	N	M	X	
2a	I	[CuCl(C ₁₉ H ₁₄ N ₃ O)] · C ₆ H ₆	213	1.93	None	1595	Calcd.	57.2	3.5	8.5	16.0	14.2
							Found	57.4	3.8	8.8	15.8	14.5
2b	I	[CuBr(C ₁₉ H ₁₄ N ₃ O)]	204	1.95	None	1594	Calcd.	51.3	3.2	9.5	14.4	18.0
							Found	51.2	3.3	9.6	14.4	17.8
2c	II	[CuCl(C ₁₉ H ₁₅ N ₄ O)] · 1.5H ₂ O	234	1.82			Calcd.	51.6	4.1		14.5	8.0
							Found	51.8	4.4		14.5	8.1
2d	III	[CuBr(C ₂₂ H ₁₅ N ₃ O)] · 1.5H ₂ O	185	1.89			Calcd.	53.7	3.9	7.8	11.9	14.9
							Found	53.9	4.3	7.7	12.0	15.1
2e	IV	[CuBr(C ₁₇ H ₁₀ N ₃ O)] · H ₂ O	241	2.01	None	1605	Calcd.	47.0	2.8	10.1	14.7	18.4
							Found	47.2	2.8	10.0	14.5	18.1
2f	V	[CuCl(C ₉ H ₁₁ N ₄ O)] · 0.5H ₂ O	220	1.85			Calcd.	36.2	4.0		21.4	11.9
							Found	36.5	4.4		21.2	11.6
2g	VI	[Cu(C ₁₉ H ₁₂ N ₃ O)OH] · 0.5H ₂ O		1.92			Calcd.	58.8	3.6	10.8	16.4	
							Found	59.4	3.7	9.1	16.2	
2h	I	[Cu(C ₁₉ H ₁₄ N ₃ O)H ₂ O](ClO ₄) · H ₂ O	160–161	1.88	None	1614	Calcd.	45.3	3.6	8.4	12.9	
							Found	45.5	3.9	8.7	13.0	
2i	VI	[Cu(C ₁₆ H ₁₂ N ₃ O)H ₂ O](ClO ₄) · H ₂ O		1.86			Calcd.	45.9	3.2	8.5	12.7	
							Found	46.2	3.4	8.0	12.4	
2j	I	[CuCl ₂ (C ₁₉ H ₁₅ N ₃ O)]	215	1.92	3310	1614	Calcd.	52.3	3.4	9.6	14.6	16.3
							Found	52.4	3.5	9.8	14.7	16.3
2k	I	[CuBr ₂ (C ₁₉ H ₁₅ N ₃ O)] · H ₂ O	156	1.96	3310	1614	Calcd.	42.0	3.1	7.7	11.8	29.5
							Found	42.5	3.2	7.7	12.0	29.8

^a Names of compounds: 2a, chloro[benzilmono-(2-pyridyl)hydrazonato]copper(II)-benzene; 2b, bromo[benzilmono-(2-pyridyl)hydrazonato]copper(II); 2c, chloro[benzilmono-(3-methyl-2-pyrazinyl)hydrazonato]copper(II)-1.5-water; 2d, bromo[benzilmono-(4-methyl-2-quinolyl)hydrazonato]copper(II)-1.5-water; 2e, bromo[acenaphthenequinonemono-(2-pyridyl)hydrazonato]copper(II)-1-water; 2f, chloro[biacetylmono-(3-methyl-2-pyrazinyl)hydrazonato]copper(II)-0.5-water; 2g, hydroxo[phenanthraquinonemono-(2-pyridyl)hydrazonato]copper(II)-0.5-water; 2h, [benzilmono-(2-pyridyl)hydrazonato]aquocopper(II) perchlorate-1-water; 2i, [phenanthraquinonemono-(2-pyridyl)hydrazonato]aquocopper(II) perchlorate-1-water; 2j, dichloro[benzilmono-(2-pyridyl)hydrazono]copper(II); 2k, dibromo[benzilmono-(2-pyridyl)hydrazono]copper(II)-1-water. 2a, 2b, and 2d were recrystallized from benzene; 2c, 2e, 2f, and 2h from a 50% ethanol-water mixture; 2i from ethanol; 2g, 2j, and 2k were not recrystallized. The first six (2a–2f) were prepared by method 2, 2h and 2i were prepared by method 1, and 2j and 2k by method 6. All were nonelectrolytes except 2h and 2i whose conductivities in nitrobenzene at 25° were 22.7 and 24.6 reciprocal ohms, respectively.

(8) A solution of the ligand (2 moles) in ethanol was treated with aqueous nickel(II) chloride (1 mole) solution containing an excess of ammonium thiocyanate. The product was precipitated.

(9) As for 8 but using a large excess of ligand (approximately 5 moles).

(10) Dry ethanol solutions of copper(II) chloride (anhydrous, 1 mole) and the ligand (2 moles) were mixed. The product crystallized slowly on standing.

(11) Solutions of the ligand (3 moles) and the metal perchlorate (1 mole) in ethanol were mixed. The product was recrystallized from aqueous ethanol.

(12) An aqueous ethanolic solution of the corresponding charged complex was treated with 5% sodium hydroxide solution and the solution extracted with benzene. The product was recovered from the benzene and recrystallized from aqueous ethanol.

(13) An aqueous solution of the complex nickel(II) perchlorate was treated with excess 5 N ammonium hydroxide solution. The bright yellow precipitate was recrystallized from 95% ethanol.

Discussion

(I) **Copper.**—Each of the ligands I–VI will react in neutral solution with copper(II) salts to give complexes of the type [Cu(Lig)X]⁰ (X = Cl, Br, or OH) or of the type [Cu(Lig)H₂O](ClO₄) in each of which the ligand residue has been deprotonated (Table II). However, if the preparations are carried out in slightly acid solution neutral compounds of the type [Cu(HLig)X₂]⁰ (X = Cl or Br) are obtained in which the ligand residue remains

protonated and probably functions only as a bidentate group. Such protonated compounds readily undergo deprotonation. They cannot even be recrystallized without undergoing some deprotonation. Thus, solution of the brown [Cu(HLig)Cl₂] in 95% ethanol yields a red solution indistinguishable from the red solution of [Cu(Lig)Cl] and it is this latter substance which crystallizes out. The same is true for water or acetone solutions. Ultraviolet and visible spectra of ethanolic solutions of [Cu(Lig)Cl] and [Cu(HLig)Cl₂] are virtually identical. So are those for the pair [Cu(Lig)Br] and [Cu(HLig)Br₂] (Table III). Thus, in neutral or alkaline polar solvents the complexed ligand is readily deprotonated. Further evidence of ligand deprotonation is given by the presence of N–H bands in the infrared spectra of the protonated compounds and their absence from the spectra of the deprotonated complexes (Table II).

(II) **Nickel.**—No less than four different types of nickel(II) coordination compounds have been obtained

TABLE III
ABSORPTION PEAKS IN ETHANOL

Compound	λ_{\max} , m μ	ϵ_0
[Cu(Lig)Cl]	503	2.34×10^4
[Cu(HLig)Cl ₂]	503	2.21×10^4
[Cu(Lig)Br]	502	2.57×10^4
[Cu(HLig)Br ₂]	503	2.50×10^4

TABLE IVa
NICKEL(II) COMPLEXES $[\text{Ni}(\text{Lig})_2]^{0a}$

Compd. no.	Ligand	Formula	M.p., °C.	Magnetic moment, B.M.	Infrared band, cm^{-1} C=O	Analyses, %				
						C	H	N	M	
4a	I	$[\text{Ni}(\text{C}_{38}\text{H}_{28}\text{N}_6\text{O}_2)] \cdot 2\text{H}_2\text{O}$	145	2.62	1592	Calcd.	65.7	4.6	12.4	8.0
						Found	65.8	4.6	12.3	8.3
4b	II	$[\text{Ni}(\text{C}_{38}\text{H}_{30}\text{N}_6\text{O}_2)]$	>300	2.60		Calcd.	66.2	4.4	16.2	8.6
						Found	66.0	4.0	16.5	8.6
4c	III	$[\text{Ni}(\text{C}_{48}\text{H}_{36}\text{N}_6\text{O}_2)]$	295	2.58	1600	Calcd.	72.2	4.5	10.5	7.4
						Found	71.7	4.6	10.5	7.3
4d	IV	$[\text{Ni}(\text{C}_{34}\text{H}_{20}\text{N}_6\text{O}_2)] \cdot 0.5\text{H}_2\text{O}$	>300	2.65	1605	Calcd.	65.6	3.4	13.5	9.5
						Found	65.3	3.5	13.3	9.6
4e	V	$[\text{Ni}(\text{C}_{18}\text{H}_{22}\text{N}_6\text{O}_2)]$	>300	2.59	1608	Calcd.	49.0	5.0	25.4	13.4
						Found	49.0	4.9	25.6	13.2
4f	VI	$[\text{Ni}(\text{C}_{38}\text{H}_{24}\text{N}_6\text{O}_2)] \cdot \frac{1}{3}\text{C}_6\text{H}_6$		2.70		Calcd.	70.9	3.9		8.5
						Found	71.0	4.2		8.4

^a Names of compounds: 4a, bis(benzilmono-2-pyridylhydrazonato)nickel(II)-2-water; 4b, bis[benzilmono-(3-methyl-2-pyrazinyl)hydrazonato]nickel(II); 4c, bis[benzilmono-(4-methyl-2-quinolyl)hydrazonato]nickel(II); 4d, bis[acenaphthenequinonemono-2-pyridylhydrazonato]nickel(II)-0.5-water; 4e, bis[bisacetylmono-(3-methyl-2-pyrazinyl)hydrazonato]nickel(II); 4f, bis[phenanthraquinonemono-2-pyridylhydrazonato]nickel(II)- $\frac{1}{3}$ -benzene. The first 4 compounds were prepared by methods 1 and 4; compounds 4e and 4f by method 1. All these substances were nonelectrolytes. None exhibited N-H bands in the infrared spectra.

TABLE IVb
NICKEL(II) COMPLEXES $[\text{NiX}(\text{HLig})(\text{Lig})]^{0a}$

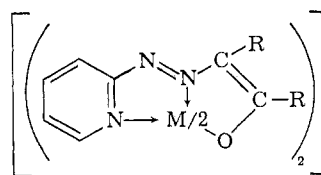
Compd. no.	Ligand	Formula	M.p., °C.	Magnetic moment, B.M.	Infrared bands, cm^{-1} C=O	Analyses, %					
						C	H	N	M	X	
4g	I	$[\text{NiCl}(\text{C}_{38}\text{H}_{28}\text{N}_6\text{O}_2)]$	245	2.65	1595	Calcd.	65.7	4.2	12.1	8.5	5.1
						Found	65.8	4.3	12.4	8.5	4.9
4h	I	$[\text{NiBr}(\text{C}_{38}\text{H}_{28}\text{N}_6\text{O}_2)] \cdot 4\text{H}_2\text{O}$	233	2.72	1592	Calcd.	56.3	4.6	10.4	7.3	9.8
						Found	56.7	5.0	10.5	7.2	10.2
4i	III	$[\text{NiCl}(\text{C}_{48}\text{H}_{37}\text{N}_6\text{O}_2)]$	>300	2.62	1602	Calcd.	69.8	4.5	10.2	7.2	4.3
						Found	70.1	4.5	10.0	7.2	4.0
4j	III	$[\text{NiBr}(\text{C}_{48}\text{H}_{37}\text{N}_6\text{O}_2)]$	>300	2.71	1606	Calcd.	66.5	4.3		6.8	9.2
						Found	66.3	4.2		7.0	9.3
4k	IV	$[\text{NiCl}(\text{C}_{34}\text{H}_{21}\text{N}_6\text{O}_2)] \cdot \text{H}_2\text{O}$	>300	2.70	1607	Calcd.	62.3	3.5	12.8	9.0	5.4
						Found	62.7	3.7	12.9	9.1	5.2
4l	IV	$[\text{NiBr}(\text{C}_{34}\text{H}_{21}\text{N}_6\text{O}_2)]$	>300	2.68	1605	Calcd.	59.5	3.1	12.2	8.6	11.6
						Found	59.2	3.6	12.2	8.5	11.8

^a Names of compounds: 4g, chloro(benzilmono-2-pyridylhydrazono)(benzilmono-2-pyridylhydrazonato)nickel(II); 4h, bromo(benzilmono-2-pyridylhydrazono)(benzilmono-2-pyridylhydrazonato)nickel(II)-4-water; 4i, chloro[benzilmono-(4-methyl-2-quinolyl)hydrazono][benzilmono-(4-methyl-2-quinolyl)hydrazonato]nickel(II); 4j, bromo[benzilmono-(4-methyl-2-quinolyl)hydrazono][benzilmono-(4-methyl-2-quinolyl)hydrazonato]nickel(II); 4k, chloro[acenaphthenequinonemono-(2-pyridyl)hydrazono][acenaphthenequinonemono-(2-pyridyl)hydrazonato]nickel(II)-1-water; 4l, bromo[acenaphthenequinonemono-(2-pyridyl)hydrazono][acenaphthenequinonemono-(2-pyridyl)hydrazonato]nickel(II). All were prepared by method 2. All were nonelectrolytes.

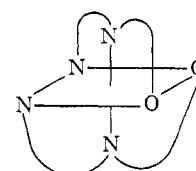
from the ligands I-VI and nickel(II) salts. They can be classified as follows. Type 1: neutral complexes containing two deprotonated ligand residues coordinated to each nickel atom, of the type $[\text{Ni}(\text{Lig})_2]^{0}$ (Table IVa). Type 2: neutral complexes containing coordinated to the nickel atom two ligand residues only one of which has been deprotonated and, additionally, an anion (Cl or Br), of the type $[\text{Ni}(\text{HLig})(\text{Lig})\text{X}]^{0}$ (Table IVb). Type 3: neutral complexes containing coordinated to the nickel atom *one* protonated ligand residue and two thiocyanate ions, of the type $[\text{Ni}(\text{HLig})(\text{NCS})_2]^{0}$ (Table IVc). Type 4: neutral complexes containing coordinated to the nickel atom two ligand residues each of which remains protonated and, additionally, *two* thiocyanate groups, of the type $[\text{Ni}(\text{HLig})_2(\text{NCS})_2]^{0}$ (Table IVd).

The compounds of the first of these types are prepared by interaction of the ligand (2 molecular pro-

portions) with nickel(II) perchlorate in aqueous alcohol. They are organic-solvent-soluble, nonelectrolyte octahedral nickel(II) complexes with slightly lower than usual magnetic moments of 2.58-2.70 B.M. and are distinguished by the absence of N-H bands from their infrared spectra. They possess intense red colors and have molecular extinction coefficients in excess of 10^4 both in aqueous ethanol and nitrobenzene solutions. They should undoubtedly be formulated as VIIa and VIIb in which each of the two tridentate residues is planar.



VIIa



VIIb

TABLE IVc
NICKEL(II) COMPLEXES $[\text{Ni}(\text{HLig})(\text{NCS})_2]^{0a}$

Compd. no.	Ligand	Formula	M.p., °C.	Magnetic moment, B.M.	Infrared bands, cm.^{-1}		Analyses, %			
					N—H	C=O	C	H	N	M
4m	I	$[\text{Ni}(\text{NCS})_2(\text{C}_{15}\text{H}_{15}\text{N}_3\text{O})]$	269	3.03	3317	1614	Calcd. 50.4	3.2	14.7	12.4
							Found 50.6	3.3	14.9	12.4
4n	III	$[\text{Ni}(\text{NCS})_2(\text{C}_{25}\text{H}_{19}\text{N}_3\text{O})] \cdot 4\text{H}_2\text{O}$	270 dec.	3.05	3311	1620	Calcd. 50.2	4.3	11.3	9.4
							Found 50.6	4.7	11.2	9.6
4o	IV	$[\text{Ni}(\text{NCS})_2(\text{C}_{17}\text{H}_{11}\text{N}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$	250 dec.	3.12	3200	1625	Calcd. 48.9	2.6	15.0	12.6
							Found 48.8	3.0	15.2	12.3
4p	V	$[\text{Ni}(\text{NCS})_2(\text{C}_9\text{H}_{12}\text{N}_4\text{O})]$	180 dec.	3.08	3350	1628	Calcd. 36.0	3.3	22.9	16.1
							Found 36.0	3.2	22.3	16.0

^a Names of compounds: 4m, bithiocyanato(benzilmono-2-pyridylhydrazone)nickel(II); 4n, bithiocyanato[benzilmono-(4-methyl-2-quinolyl)hydrazone]nickel(II)-4-water; 4o, bithiocyanato(acenaphthenequinonemono-2-pyridylhydrazone)nickel(II)-0.5-water; 4p, bithiocyanato[biacetylmono-(3-methyl-2-pyrazinyl)hydrazone]nickel(II). All were prepared by method 8. Conductivities in nitrobenzene were (reciprocal ohms): 4m, 2.4; 4n, 8.5; 4o, 6.2; 4p, 6.4. In nitromethane the conductivity of 4m was 15.2 reciprocal ohms and that of 4n, 61.2 reciprocal ohms.

TABLE IVd
NICKEL(II) COMPLEXES $[\text{Ni}(\text{HLig})_2(\text{NCS})_2]^{0a}$

Compd. no.	Ligand	Formula	M.p., °C.	Magnetic moment, B.M.	Infrared bands, cm.^{-1}		Analyses, %			
					N—H	C=O	C	H	N	N
4q	I	$[\text{Ni}(\text{NCS})_2(\text{C}_{38}\text{H}_{30}\text{N}_6\text{O}_2)]$	300	3.11	3240	1614	Calcd. 61.8	4.3	14.4	7.6
							Found 62.1	4.3	14.0	7.5
4r	V	$[\text{Ni}(\text{NCS})_2(\text{C}_{13}\text{H}_{24}\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$	180 dec.	3.20	3308	1620	Calcd. 40.3	4.7	23.5	9.9
							Found 40.1	4.3	23.2	9.7

^a Names of compounds: 4q, bithiocyanatobis(benzilmono-2-pyridylhydrazone)nickel(II); 4r, bithiocyanatobis[biacetylmono-(3-methyl-2-pyrazinyl)hydrazone]nickel(II)-2-water. Both were prepared by method 9. Conductivities at 25° in nitrobenzene were (reciprocal ohms): 4q, 3.1; 4r, 6.3.

The nickel(II) complexes of type 2 (Table IVb) are prepared by interaction of an ethanolic solution of the ligand with an aqueous solution of nickel(II) halide. They possess deep red colors similar to those of the type I compounds, are soluble in organic solvents, and are nonelectrolytes in nitrobenzene solution. If each ligand residue is regarded as bonded to the metal atom at each of its three potential donor atoms, and the halogen is also bonded to the metal, it would be necessary to formulate the nickel as seven-covalent. The magnetic moments of the complexes, however, are normal for an octahedral ligand field. Acceptance of six-coordination with halogen as one donor makes it necessary to assume that one of the ligand residues is protonated and functioning only as a bidentate chelating group. Unfortunately, the infrared spectra of all the compounds of this type are difficult to interpret in the 3μ region. Even when dilute solutions (to minimize hydrogen bonding) and high resolutions were used no clear-cut N—H peaks were obtained. At the same time it does not appear possible to say with certainty—as it is for the spectra of the compounds of type I—that N—H peaks are absent. It did not appear, either, that OH peaks were present in the spectra of type 2 compounds. Their ultraviolet and visible spectra in either nitrobenzene or 95% ethanol were slightly different from those of the corresponding type I compounds (Table V).

The coordinated halogen atom is not readily lost from these compounds, which can be recrystallized from polar solvents. Addition of alkali (to about 1%) to solutions of the complex $[\text{Ni}(\text{HLigI})(\text{LigI})\text{Br}]$ in 95% aqueous ethanol produced no change in the ul-

TABLE V
VISIBLE PEAKS AND MOLECULAR EXTINCTION COEFFICIENTS FOR THE Ni(II) COMPOUNDS OF LIGAND I IN 95% AQUEOUS ETHANOL AND IN NITROBENZENE

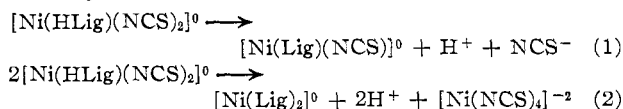
Solvent	Compound	λ_{max} , $m\mu$	ϵ
Ethanol	$[\text{Ni}(\text{LigI})_2]^{0}$	492	4.11×10^4
Ethanol	$[\text{Ni}(\text{LigI})(\text{HLigI})\text{Cl}]$	478	1.91×10^4
Ethanol	$[\text{Ni}(\text{LigI})(\text{HLigI})\text{Br}]$	478	2.54×10^4
Ethanol	$[\text{Ni}(\text{HLigI})(\text{NCS})_2]$	492	2.06×10^4
Ethanol	$[\text{Ni}(\text{HLigI})_2(\text{NCS})_2]$	492	4.04×10^4
Nitrobenzene	$[\text{Ni}(\text{LigI})_2]$	492	3.38×10^4
Nitrobenzene	$[\text{Ni}(\text{LigI})(\text{HLigI})\text{Cl}]$	478	2.12×10^4
Nitrobenzene	$[\text{Ni}(\text{HLigI})(\text{NCS})_2]$	490	5.17×10^2
		422	4.84×10^2
Nitrobenzene	$[\text{Ni}(\text{HLigI})_2(\text{NCS})_2]$	483	1.25×10^2

traviolet or visible absorption spectra. This would appear to indicate that deprotonation is not easy. However, treatment with hot 5 N sodium hydroxide solution gave the fully deprotonated $[\text{Ni}(\text{LigI})_2]^{0}$ compound.

The nickel(II) complexes of type 3 (Table IVc) precipitate when an aqueous solution of nickel(II) chloride (1 mole) containing excess ammonium thiocyanate is added to an ethanolic solution of the ligand (2 moles). The formula $[\text{Ni}(\text{HLig})(\text{NCS})_2]^{0}$ closely resembles the $[\text{Cu}(\text{HLig})\text{X}_2]$ (where X = Cl or Br) formula of certain of the copper(II) complexes. Because of their low solubilities in nitrobenzene molecular weight determinations could not be carried out cryoscopically using this solvent. There is the possibility that they can be formulated as salts, $[\text{Ni}(\text{HLig})_2]^{+2}[\text{Ni}(\text{NCS})_4]^{-2}$. Although salts containing the $[\text{Ni}(\text{NCS})_4]^{-2}$ anion and a simple cation do not

appear to have been isolated, Nyholm and Gill⁵ have measured the magnetic moment of the tetrahedral nickel atom in the $[\text{NiX}_4]^{-2}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) anions and found values of 3.4–4.0 B.M. The $[\text{Ni}(\text{NCS})_4]^{-2}$ anion might well be expected to have a moment in this range. If the compounds of type 3 do contain complex cations with two *protonated* ligand groups each of which supplies three donor atoms to help provide an octahedral environment for the nickel(II) atom, their moments might be expected to lie in the normal range 3.0–3.4 B.M. The salt-like structure with a mean value for the magnetic moment of each nickel atom (cationic and anionic) would still lead to an expectation of somewhat higher magnetic moments than has been observed.

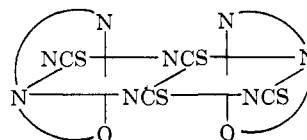
Conductivity measurements in nitrobenzene would seem to indicate that the main species present is the monomer, unless thiocyanate bridging has occurred, but that some dissociation has taken place in solution. This dissociation may be formulated as occurring in two ways



As in ethanol solution the ultraviolet and visible spectra of the compound $[\text{Ni}(\text{HLigI})(\text{NCS})_2]$ are identical with the corresponding spectra of $[\text{Ni}(\text{LigI})_2]$, it would appear to be the second dissociation which is occurring. This is supported by the conductivity of $[\text{Ni}(\text{HLigI})(\text{NCS})_2]$ in ethanol ($\Lambda_{1000/25} = 250$ reciprocal ohms). The dependence of this dissociation upon the polarity of the solvent is indicated by the conductivities of some of the type 3 compounds in nitromethane (Table IVc). In this solvent the dissociation is greater than in nitrobenzene but less than in ethanol. Further confirmation is to be obtained by comparison of the visible absorption spectra of nitrobenzene solutions. That of $[\text{Ni}(\text{LigI})_2]^0$ has only one peak while that of $[\text{Ni}(\text{HLigI})(\text{NCS})_2]^0$ has two peaks with greatly lowered Σ_0 values (Table V). The change in color of the yellow thiocyanato compounds of type 3 on solution in water, alcohol, or acetone to the characteristic red color of the $[\text{Ni}(\text{Lig})_2]^0$ compounds indicates the ease of proton removal in polar solvents when excess ammonium thiocyanate is not present. This ease of breakdown, together with the possibility of obtaining pure compounds in the initial preparations, discouraged any attempts at recrystallization.

The covalent bonding of both NCS groups in the type 3 compounds is supported by the infrared peaks recorded in Table VI. The peak at approximately 2080 cm^{-1} has been shown in many studies to be indicative of nickel tetraammine complexes with a *trans* thiocyanate octahedral structure, the two thiocyanate groups being bonded through nitrogen.^{6–8} The higher

bands in these spectra could indicate that thiocyanate bridging has occurred and that the compounds are nonelectrolyte dimers with some such structure as VIII.



VIII

TABLE VI

INFRARED THIOCYANATE PEAKS FOR THE Ni(II) COMPOUNDS OF TABLE IVc: $[\text{Ni}(\text{HLig})(\text{NCS})_2]$

Ligand	Compound	NCS peaks, cm^{-1}
I	$[\text{Ni}(\text{HLigI})(\text{NCS})_2]$	2088, 2107
II	$[\text{Ni}(\text{HLigII})(\text{NCS})_2]$	2080, 2100
V	$[\text{Ni}(\text{HLigV})(\text{NCS})_2]$	2080, 2115
VI	$[\text{Ni}(\text{HLigVI})(\text{NCS})_2]$	2080, 2120

The infrared spectrum of the compound $[\text{Ni}(\text{terpyridine})(\text{NCS})_2]^0$ is of interest here as it also shows peaks at 2098 and 2122 cm^{-1} .⁹ It would appear unlikely on theoretical grounds¹⁰ that the molecules of any of these nickel(II) complexes have monodentate thiocyanate groups bonded to the nickel atoms through sulfur as might be suggested by the frequency of the absorption.

The nickel(II) complexes of type 4, $[\text{Ni}(\text{HLig})_2(\text{NCS})_2]^0$, Table IVd, are prepared by treating an ethanolic solution of excess ligand with aqueous nickel(II) chloride solution containing excess ammonium thiocyanate. They are almost nonconducting in nitrobenzene and have magnetic moments commensurate with two unpaired electrons for each nickel atom. Their molecules contain two ligand residues each of which remains protonated, as is indicated by the presence of NH bonds in the infrared spectra and the presence of the two thiocyanato groups in the neutral molecules. When dissolved, *e.g.*, in 98% aqueous ethanol, they show much the same dissociation pattern exhibited by the type 3 compounds. Thus, the compound $[\text{Ni}(\text{HLigI})_2(\text{NCS})_2]^0$ shows a similar absorption peak (at 492 $m\mu$, ϵ_0 2.04×10^4) to $[\text{Ni}(\text{LigI})_2]$ (ϵ_0 4.11×10^4 at 492 $m\mu$). Further, the former compound possesses, in this solvent, a conductivity, Λ_{1000} , of 243 reciprocal ohms at 25°. Similarly to the type 3 compounds these bluish pink complexes give red solutions in alcohol, water, and acetone and cannot readily be recrystallized from these solvents without decomposition into uncharged complexes of type I. The single infrared thiocyanato band for these complexes (at 2085 cm^{-1} for $[\text{Ni}(\text{HLigI})_2(\text{NCS})_2]$ and at 2080 cm^{-1} for $[\text{Ni}(\text{HLigV})_2(\text{NCS})_2]$) indicates covalent bonding of both thiocyanate groups to the nickel through the nitrogen atom.^{8–10} As only one band is obtained in the C=N stretching region for these compounds at the position expected for normal co-

(5) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(6) E. C. Lingafelter, *Nature*, **182**, 1730 (1958).

(7) C. Pecile, G. Giacometti, and A. Turco, *R.C. Acad. Ital.*, **28**, 189 (1960).

(8) C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, **19**, 372 (1961).

(9) T. N. Lockyer, Thesis, University of N. S. Wales, 1962.

(10) J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

TABLE VII
Pd(II), Na(I), Mn(II), AND Au(III) COMPLEXES^a

Compd. no.	Formula	Method	Color	M.p., °C.	Analyses, %					
					C	H	N	M	X	
7a	[Pd(C ₁₅ H ₁₄ N ₃ O)Cl]	3	Red-blue	>300	Calcd.	51.6	3.2	9.5	24.2	8.0
					Found	51.5	3.3	8.6	24.0	8.1
7b	[Pd(C ₁₇ H ₁₀ N ₃ O)Cl]·2H ₂ O	3	Red-blue	>300	Calcd.	45.3	3.1	9.3	23.5	7.9
					Found	45.6	3.0	9.1	23.4	7.6
7c	[Na(C ₃₈ H ₂₃ N ₆ O ₂)]·H ₂ O	7	Bright red	128	Calcd.	71.0	4.8	13.1	3.6	...
					Found	70.7	5.0	13.0	3.4	...
7d	[Mn(C ₃₃ H ₂₃ N ₆ O ₂)]·H ₂ O	1	Red-green	>300	Calcd.	66.2	3.6	13.6	8.9	...
					Found	65.8	4.2	11.7	8.8	...
7e	[Au(C ₁₉ H ₁₄ N ₃ O)Cl][AuCl ₄]·H ₂ O	3	Yellow	108	Calcd.	23.6	1.8	4.8	22.4	20.2
					Found	23.2	2.0	5.2	22.2	19.8

^a The names of these compounds are: 7a, chlorobenzilmono-(2-pyridylhydrazonato)palladium(II); 7b, chloroacenaephthenequinone-mono-(2-pyridylhydrazonato)palladium(II)-2-water; 7c, benzilmono-(2-pyridylhydrazono)benzilmono-(2-pyridylhydrazonato)sodium(I)-1-water; 7d, bis[benzilmono-(2-pyridylhydrazonato)]manganese(II)-1-water; 7e, chlorobenzilmono-(2-pyridylhydrazonato)-gold(III) tetrachloroaurate(III)-1-water. All were diamagnetic except compound 7d (6.01 B.M.). All were nonelectrolytes except 7e, which had a conductivity of 24.6 reciprocal ohms in nitrobenzene at 25°. Compound 7a exhibited no infrared N—H bands but a carbonyl peak at 1588 cm.⁻¹ Compound 7c had an infrared N—H band at 3310 cm.⁻¹ and a C=O band at 1590 cm.⁻¹.

TABLE VIII
COMPLEXES FROM BENZALDEHYDE-(2-PYRIDYL)HYDRAZONE^a

Compd. no.	Formula	Method	Color	M.p., °C.	Magnetic moment, B.M.	Analyses, %				
						C	H	N	M	
8a	[Cu(C ₁₂ H ₁₁ N ₃)Cl ₂]	10	Olive-green	145		Calcd.	43.4	3.3	12.7	19.2
						Found	42.7	3.4	12.0	18.9
8b	[Co(C ₃₆ H ₃₃ N ₉)](ClO ₄) ₂ ·H ₂ O	11	Yellow-brown	170	5.01	Calcd.	49.7	4.0	14.5	6.8
						Found	49.8	3.9	13.4	6.6
8c	[Ni(C ₃₆ H ₃₃ N ₉)](ClO ₄) ₂ ·H ₂ O	11	Yellow-brown	185	3.12	Calcd.	49.8	4.0	14.5	6.8
						Found	50.0	3.8	13.4	6.9
8d	[Cu(C ₁₂ H ₁₀ N ₃)Cl]	12	Cream	146-147	1.65	Calcd.	48.8	3.4		
						Found	48.6	3.3		
8e	[Co(C ₂₄ H ₂₀ N ₆)(H ₂ O) ₂]	12	Dark brown	140-141	4.93	Calcd.	59.2	4.9	17.3	12.1
						Found	59.2	4.8	16.8	12.0
8f	[Ni(C ₂₄ H ₂₀ N ₆)(NH ₃)]·2.5H ₂ O	13	Yellow	136-137	3.02	Calcd.	54.3	5.8		11.1
						Found	54.2	5.2		11.0

^a The names of these compounds are: 8a, dichloro(benzaldehyde-2-pyridylhydrazono)copper(II); 8b, tris(benzaldehyde-2-pyridylhydrazono)cobalt(II) perchlorate-1-water; 8c, tris(benzaldehyde-2-pyridylhydrazono)nickel(II) perchlorate-1-water; 8d, chloro-(benzaldehyde-2-pyridylhydrazonato)diamminenickel(II)-2.5-water. Compound 8c had a molecular conductivity in nitrobenzene at 25° of 81.2 reciprocal ohms. Compounds 8a, 8d, 8e, and 8f were nonelectrolytes. Infrared bands for N—H were as follows: 8a, 3230; 8b, 3235; 8c, 3238; and 8f, 3225 cm.⁻¹. Compounds 8d and 8e lacked such bands.

valently bonded isothiocyanate groups, it seems reasonable to assume that both thiocyanate groups are bonded only to one nickel atom and that the compounds are monomers.

These type IV compounds are nonelectrolytes in nitrobenzene. If it is assumed that each ligand molecule is functioning as a tridentate residue when complexed it must then be concluded that the nickel atom is eight-covalent. The properties of the compounds strongly suggest that they are normal octahedral nickel(II) complexes. It must then be concluded that each ligand residue when protonated functions only as a bidentate ligand. When deprotonation occurs the ligands become planar tridentate groups. The distal nitrogen atom of the heterocyclic hydrazine residue must always be a donor atom when the ligand is coordinated. When the ligand remains protonated and functions only as a bidentate ligand the second bonded donor atom would appear to be the pyridine nitrogen atom. Support for this conclusion can be obtained from the following facts: (1) The hydrazones derived from simple carbonyl compounds and N-heterocyclic hydrazine of the amidrazone type (*e.g.*,

benzaldehyde-2-pyridylhydrazono) function as bidentate chelating agents and yield coordination compounds which are capable of deprotonation (Table VIII). (2) Application of the method devised to prepare the complexes [Ni(HLig)(NCS)₂]⁰ to ligand VI gave only a solution characterized by the deep red color of the deprotonated complex. Addition of acid to this solution led only to slow deposition of phenanthraquinone (m.p. 206°). Thus, an attempt to force a proton onto nitrogen leads to breakdown of the ligand. (3) The carbonyl band in the infrared spectrum of complexes where the ligand residue remains protonated suffers less change in position from that exhibited by the ligand itself than does the carbonyl band exhibited by the deprotonated complexes (Table IX). This would appear to indicate that in the protonated complexes the carbonyl oxygen atom is not functioning as a donor atom in the same way as it does in the deprotonated complexes. Mixed compounds of the type [Ni(Lig)(HLig)X] show only the carbonyl band typical of the fully deprotonated complexes. The lower frequency of the band in these latter complexes would appear to be due to formation

TABLE IX^aCARBONYL INFRARED (NUJOL) PEAKS (CM.⁻¹) OF LIGANDS AND Cu(II) AND Ni(II) COMPOUNDS

Compound	Ligand			
	I	II	V	VI
Ligand	1632	1645	1642	1632
[Ni(Lig) ₂]	1592	1605	1608	1600
[Cu(Lig)Cl]	1595	1605	N.d. ^b	N.d. ^b
[Cu(HLig)Cl ₂]	1614	N.d. ^b	N.p. ^c	N.p. ^c
[Ni(Lig)(HLig)Cl]	1595	1607	N.p. ^c	1602
[Ni(Lig)(HLig)Br]	1592	1605	N.p. ^c	1606
[NiH(Lig)(NCS) ₂]	1614	1625	1628	1620
[Ni(HLig) ₂ (NCS) ₂]	1614	N.p. ^c	1620	N.p. ^c

^a See also Tables I-III. ^b Indicates spectrum not done (N.d.). ^c Indicates compound not prepared (N.p.).

of resonating chelate ring systems involving all three donor atoms and thus lowering the double bond character of the carbonyl group.

Other Metals.—Complexes derived from one or the other of the ligands I-VI with salts of some metals other than those discussed so far are listed together in Table VII. Complexes derived from cobalt and iron salts will be discussed in a later paper.

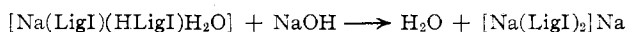
The palladium(II) and gold(III) complexes are apparently square-planar compounds, as demonstrated by their magnetic moments. For each of them the infrared spectrum of the compound shows no amine or normal carbonyl bands, indicating deprotonation upon coordination. The manganese(II) complex noted in Table VII is a high-spin octahedral complex.

The complex sodium compound (Table VII) is of considerable interest. Six-coordinate compounds of sodium have been previously reported by Sidgwick and Brewer¹¹ among others. In the compounds listed by them the six donor atoms are oxygen. The present compound is readily prepared from ligand I and sodium hydroxide in aqueous solution and can be readily extracted into and recovered from benzene. Its infrared spectrum exhibits both N-H and C=O bands, indicating that one of the two complexed ligand residues retains its proton. If it is true that such a protonated residue would function only as a bidentate chelate group it is conceivable (with the deprotonated residue occupying three coordination sites) that the remaining (sixth) position of the coordination octa-

(11) F. M. Brewer and N. V. Sidgwick, *J. Chem. Soc.*, **127**, 2379 (1925).

hedron is filled by the molecule of water present. Such coordination of water in sodium complexes is well known.¹²

The lowering of the carbonyl band frequency to 1590 cm.⁻¹ upon coordination is typical of carbonyl complex compounds, such as the acetylacetonato complexes.¹³ In the visible the position of the absorption maximum [at 484 m μ (ϵ_0 3.49 \times 10³)] exhibited by the ligand I in ethanol solution is altered by addition of sodium hydroxide solution. The compound [Na(LigI)(HLigI)H₂O] has a peak at 478 m μ (ϵ_0 1.52 \times 10⁴). If either of these compounds is examined in ethanol solution made approximately 0.25 *N* alkaline with sodium hydroxide the peak occurs at 473 m μ (ϵ_0 1.13 \times 10⁴). This suggests that in alkaline solution the second ligand I residue is also deprotonated according to the equation



Many of the deprotonated compounds discussed above are intensely colored and are often dichroic. The intensity of color only occurs on proton loss. Where protons still remain attached to the coordinated ligand residues, as in the copper(II) and nickel(II) complexes of the types [M(HLig)X₂], where X = Cl, Br, or NCS, and [Ni(HLig)₂(NCS)₂], the intense color is lacking. When proton removal is effected and resonating azophenol-metal type rings are produced in the complex molecules high solubility in solvents such as alcohol, acetone, benzene, and chloroform and intense red color become apparent. It is noteworthy that deprotonation of complexes containing benzaldehyde-2-pyridylhydrazone residues does not lead to such intense colors. Here, the system of three fused resonant rings is not present.

Acknowledgments.—The authors gratefully acknowledge a grant (919-A1) from the Petroleum Research Fund of the American Chemical Society, which has made this work possible, and the assistance of Miss B. Stevenson for all the organic microanalyses and spectra recorded.

(12) Cf. J. C. Bailar, Jr., "The Chemistry of Coordination Compounds, Reinhold Publishing Co., New York, N. Y., 1956, p. 2.

(13) Cf. L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1958, pp. 145-146.