num, was formed. It appears to be $PtCl_2Br_2C_2H_4$ (%Pt = 43.00) formed by reaction 6

$$PtCl_2C_2H_4 + Br_2 \longrightarrow PtCl_2Br_2C_2H_4 \quad (6)$$

Chatt[6] obtained $PtCl_4C_2H_4$ in the chlorination of $(PtCl_2C_2H_4)_2$ at room temperature and the symmetrical ethylene dichloride at higher temperatures. Kharasch and Ashford[10] brominated $[PtCl_2(Styrene)]_2$ and obtained the symmetrical dibromide and a red solid. In light of the above experiments with the ethylene complex, it appears that this red solid was probably $PtCl_2Br_2(CH_2CHC_6H_5)$.

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WASHINGTON, D. C.

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA FISICA DELL'UNIVERSITÀ DI FIRENZE]

Chemical Reactions of Complexes. VII. Reaction of Hydrazides and Aromatic *o*-Oxy- and *o*-Aminoaldehydes and Ketones with Nickel Acetate

BY LUIGI SACCONI

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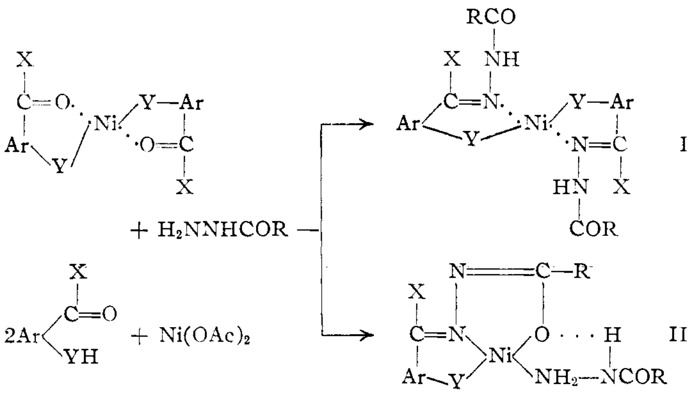
The formation of complexes by competitive reactions between aromatic *o*-oxy- and *o*-aminoaldehydes and ketones, acylhydrazines and nickel acetate has been studied, and the influence of the ligand molecules has been investigated. In the case of salicylaldehyde, the tendency to yield bicyclic planar complexes parallels the aromaticity of the acyl group and hence with the presence of an extra negative charge on the enolate oxygen atom of the carbonyl group.

Our study[1] of the reaction of hydrazides with nickel disalicylaldehyde or with nickel acetate and salicylaldehyde demonstrated the occurrence of the following competitive reactions.



Ar = C_6H_4; X = H; Y = O; R = alkyl, phenyl, phenylalkyl

According to the nature of the R group, symmetrical paramagnetic ionic complexes I or diamagnetic bicyclic planar complexes II are formed.

In the present work we have studied the behavior of the same nickel salt in aqueous alcoholic solution with hydrazides and aldehydes or ketones of the above general formula and where Ar = C_6H_4, $C_{10}H_6$; X = H, CH_3; Y = O, NH; R = alkyl, phenylalkyl, phenyl, hexahydrophenyl, naphthyl, diphenyl, 2-furyl, 3-methyl-5-isoxazolyl.

(1) Complexes of type I are formed when Ar = C_6H_4; X = H; Y = O (salicylaldehyde); and R = furylhydrazide or 3-methyl-5-isoxazolylhydrazide. When R = C_6H_{11} (hexahydrobenzhydrazide), the reaction proceeds in the direction of complex I. When R = C_6H_5–C_6H_4 (*p*-phenylbenzhydrazide), complex II is first formed; if treated with salicylaldehyde, this compound gives complex I. When R = $C_{10}H_7$ (α- and β-naphthydrazide), the reaction proceeds in the direction of complex II. In the case of α-naphthydrazide treatment with salicylaldehyde yields the corresponding complex I; this treatment has no effect on the complex from β-naphthydrazide.

From our present and published results,[1] we can list the R groups in order of their increasing tendency to yield bicyclic planar complexes as follows

A.	B.
alkyl	phenyl
arylalkyl	substituted phenyl
hexahydrophenyl	diphenyl
furyl	α-naphthyl
3-methyl-5-isoxazolyl	

C. β-naphthyl

The R groups in series A give only green paramagnetic complexes (I) with sp^3 ionic structures; those in B first yield complexes of type II which, when treated with excess salicylaldehydes, are transformed to complexes of type I; β-naphthyl yields only an orange diamagnetic complex (II) with a square-planar dsp^2 covalent structure. Roughly speaking, the tendency to form bicyclic complexes of type II increases with the aromaticity of the R group. Indeed, the increase in aromatic character of some of the R groups, from furyl to α- and β-naphthyl, parallels the resonance energy of the corresponding molecules, which increases in the following order[2]

Substance	Resonance energy, kcal./mole
Furan	23
Benzene	39
Diphenyl	47
Naphthalene	75

On the other hand the aromaticity of the R groups is paralleled with the tendency toward

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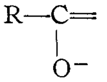
(1) L. Sacconi, THIS JOURNAL, **74**, 4503 (1952).

(2) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933); *cf.* A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 157.

enolization of the R—CO— groups,[3] *i.e.*, with the tendency of the carbonyl oxygen atom to assume an extra negative charge according to the scheme:



$$R{-}\underset{\overset{|}{O^-}}{C}{=}$$

This should reduce the effective difference in electronegativity between the nickel and the oxygen atom and hence it should favor the formation of less polar bonds. In other words, the negative charge on the oxygen will make it more able to act as an electron pair donor atom, with consequent formation of square dsp^2 bonds.

These views agree with Mellor's[4] and Nyholm's[5] on the relations between electronegativity of attached atoms and the nickel-ligand bond type.

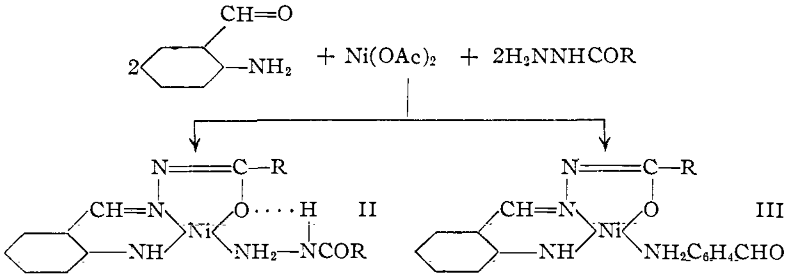
The tendency of the hydrazones to enolize would be expected to increase with the aromaticity of the R group.[3] In fact, the green complexes (I) in which R = alkyl are insoluble or very sparingly soluble in dilute sodium hydroxide solution; the complexes in which R = furyl or phenyl are soluble. Moreover, the extra negative charge assumed by the carbonyl oxygen atom in the enol form should reduce the effective difference in electronegativity between the nickel and the oxygen atom, making the latter more able to act as an electron pair donor atom, with consequent formation of square dsp^2 bonds.[4]

(2) When Ar = C_6H_4, X = CH_3, Y = O (*o*-oxyacetophenone) and R = C_6H_5 (benzhydrazide), only complex II is obtained; treatment with *o*-oxyacetophenone has no effect.

(3) Generally when Ar = $C_{10}H_6$, X = H, and Y = O (*o*-oxynaphthaldehyde), both compounds I and II are formed simultaneously, together with the green nickel di-*o*-oxynaphthaldehyde. Pure compounds are difficult to isolate.

With R = C_6H_4Cl (*o*-chlorobenzhydrazide), complex II was isolated.

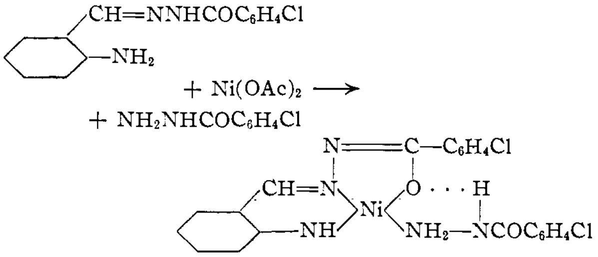
(4) The following reactions occur concurrently when Ar = C_6H_4, X = H, and Y = NH (*o*-aminobenzaldehyde).



The complexes III are deep red in color and diamagnetic, therefore planar with respect to the four dsp^2 covalent bonds.

When R = C_6H_5 (benzhydrazide), $C_6H_4NO_2$ (*m*-nitrobenzhydrazide) or C_6H_{11} (hexahydrobenzhydrazide), mostly complex III is produced.

When R = C_6H_4Cl (*p*-chlorobenzhydrazide), complex III is formed. A complex of type II is obtained by reaction of nickel acetate with *p*-chlorobenzhydrazide and the *p*-chlorobenzhydrazone of *o*-aminobenzaldehyde.



Other substituted benzhydrazides yield mixtures of complexes II and III. Symmetrical complexes of type I have not been isolated.

From these results it appears that the tendency to form symmetrical paramagnetic ionic complexes diminishes in the order salicylaldehyde > *o*-oxynaphthaldehyde > *o*-aminobenzaldehyde, *o*-oxyacetophenone.

Experimental

Complexes of type I are very sparingly soluble or insoluble in alcohol, ether, chloroform and benzene; complexes of type II are sparingly soluble in alcohol and ether; complexes of type III are extremely soluble in chloroform and ether, and soluble in alcohol.

Preparation of Complexing Agents and Complexes. 3-Methyl-5-isoxazolylhydrazide.—The ethyl ester of 3-methyl-5-isoxazoic acid (3.6 g.) and 10 g. of hydrazine hydrate in 30 ml. of alcohol were heated on a sand-bath for 2 hours. The crystalline product was filtered and recrystallized from alcohol to give needles melting at 139–140°.

Anal. Calcd. for $C_5H_7O_2N_3$: N, 29.77. Found: N, 29.85.

***o*-Aminobenzal-*p*-chlorobenzhydrazide.**—*o*-Aminobenzaldehyde and *p*-chlorobenzhydrazide in alcohol were refluxed over a water-bath. Pale yellow needles were obtained which were soluble in alcohol and ether and gave a light yellow solution in aqueous alkali, m.p. 232–234°.

Anal. Calcd. for $C_{14}H_{12}ON_3Cl$: N, 15.36; Cl, 12.96. Found: N, 15.60; Cl, 12.85.

Nickel Bis-salicylidene-α-naphthydrazide.—Nickel acetate (0.27 g.) in 5 ml. of water was mixed with 0.4 g. of α-naphthydrazide and 0.25 g. of salicylaldehyde in 25 ml. of alcohol. The mixture was warmed on a water-bath under reflux. After a few minutes 0.6 g. of salicylaldehyde was added and the mixture warmed again for one hour. A green microcrystalline powder was obtained which did not melt at 280°.

Anal. Calcd. for $C_{36}H_{26}O_4N_4Ni$: N, 8.79; Ni, 9.21. Found: N, 8.72; Ni, 9.53.

Nickel Benzhydrazide *o*-Oxyacetophenone–benzhydrazone.—Nickel acetate (1.0 g.) in 14 ml. of water was warmed on a water-bath under reflux for one hour with a solution of 1.1 g. of benzhydrazide and 0.6 g. of acetophenone in 30 ml. of alcohol (1 mole, 2 ml., 1 mole). Orange prisms were obtained which decomposed at about 250°.

Anal. Calcd. for $C_{22}H_{20}O_3N_4Ni$: N, 12.53; Ni, 13.13. Found: N, 12.54; Ni, 12.87.

Nickel *o*-Chlorobenzhydrazide *o*-Oxynaphthaldehyde-*o*-chlorobenzhydrazone.—A solution of 0.25 g. of *o*-oxynaphthaldehyde and 0.5 g. of *o*-chlorobenzhydrazide in 25 ml. of alcohol was mixed with 0.4 g. of nickel acetate in 10 ml. of alcohol. It yielded red-orange crystals which darkened at about 250°.

Anal. Calcd. for $C_{25}H_{18}O_3N_4Cl_2Ni$: N, 10.15; Ni, 10.63. Found: N, 10.00; Ni, 10.62.

Nickel *o*-Aminobenzaldehyde *o*-Aminobenzalbenzhydrazide.—*o*-Aminobenzaldehyde (0.7 g.) in 7 ml. of alcohol

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[3] *Cf.* R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934).

[4] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 475 (1940).

[5] R. S. Nyholm, *Chem. Rev.*, **53**, 275, 276 (1953).

TABLE I

THE PREPARATION OF NICKEL HYDRAZIDES FROM NICKEL DISALICYLALDEHYDE (I) AND THE APPROPRIATE HYDRAZIDE (II)[a]

Nickel hydrazide	I, g.	II, g.	Form[b]	M.p., °C.	Empirical formula	Analyses, % Nitrogen Calcd.	Analyses, % Nitrogen Found	Analyses, % Nickel Calcd.	Analyses, % Nickel Found
Bis-salicylidenefuryl	0.5	.. (25)[c]	y-g M	>300	$C_{24}H_{18}O_6N_4Ni$	10.84	11.14	11.36	11.67
Bis-salicylidene-3-methyl-5-isoxazolyl	1.0	1.0 (25)	g-y M	Dec. 300	$C_{24}H_{20}O_6N_6Ni$	15.42	15.67	10.73	10.60
Bis-salicylidenehexahydrobenz	0.5	0.5 (40)	g C	>280	$C_{28}H_{34}O_4N_4Ni$	10.20	10.49	10.68	10.66
Bis-salicylidene-*p*-phenylbenz[d]	0.3	0.5 (40)	g M	>300	$C_{40}H_{30}O_4N_4Ni$	8.13	7.98	8.51	8.49
p-Phenylbenzhydrazide salicylidene-*p*-phenylbenz	0.3	0.5 (35)	o N	Dec. 390	$C_{33}H_{26}O_3N_4Ni$	9.57	9.43	10.03	10.18
α-Naphthydrazide salicylidene-α-naphthydrazide[e]	0.5	0.72 (40)	o M		$C_{29}H_{22}O_3N_4Ni$	10.51	10.12	11.01	10.81
β-Naphthydrazide salicylidene-β-naphthydrazide	0.5	0.7 (35)	o M		$C_{29}H_{22}O_3N_4Ni$	10.51	9.98	11.01	11.30

[a] The reagents in alcohol were heated on a water-bath. [b] y, yellow; g, green; o, orange; N, needles; M, microcrystalline powder; C, crystals. [c] (ml. alcohol). [d] After the mixture was heated under reflux for a few minutes, 1 g. of salicylaldehyde was added and refluxing continued for an hour. [e] The precipitate formed was suspended in 4% sodium hydroxide solution and heated to remove the symmetrical complex.

mixed with 0.3 g. of benzhydrazide in 7 ml. of alcohol and 0.35 g. of nickel acetate in 3 ml. of water was partially evaporated on a water-bath. Deep red crystals melting with decomposition at 223° were obtained.

Anal. Calcd. for $C_{21}H_{18}O_2N_4Ni$: N, 13.43; Ni, 14.07. Found: N, 13.03; Ni, 14.25.

Nickel *o*-Aminobenzaldehyde *o*-Aminobenzalhexahydrobenzhydrazide.—A mixture of 0.2 g. of *o*-aminobenzaldehyde in 15 ml. of alcohol, 0.5 g. of hexahydrobenzhydrazide in 15 ml. of alcohol and 0.5 g. of nickel acetate in 10 ml. of water was heated on a water-bath for 15 minutes. Deep red needles melting with decomposition at 192° were obtained.

Anal. Calcd. for $C_{21}H_{24}O_2N_4Ni$: N, 13.24; Ni, 13.87. Found: N, 13.73; Ni, 13.96.

Nickel *p*-Chlorobenzhydrazide *o*-Aminobenzal-*p*-chlorobenzhydrazide.—A mixture of 0.35 g. of *p*-chlorobenzhydrazide in 7 ml. of alcohol, 0.5 g. of nickel acetate in 10 ml. of alcohol and 0.5 g. of *o*-aminobenzal-*p*-chlorobenzhydrazide in 15 ml. of alcohol was heated on a water-bath. Orange needles melting with decomposition at about 307° were obtained.

Anal. Calcd. for $C_{21}H_{17}O_2N_5Cl_2Ni$: N, 13.98; Ni, 11.71; Cl, 14.15. Found: N, 13.66; Ni, 11.72; Cl, 14.08; (Ni:Cl = 1:2).

Nickel *o*-Aminobenzaldehyde *o*-Aminobenzal-*p*-chlorobenzhydrazide.—A mixture of 0.75 g. of *o*-aminobenzaldehyde in 5 ml. of alcohol, 0.4 g. of *p*-chlorobenzhydrazide in 10 ml. of alcohol and 0.6 g. of nickel acetate in 5 ml. of alcohol was warmed on a water-bath. The precipitate was recrystallized from dioxane and alcohol to yield deep red needles.

Anal. Calcd. for $C_{21}H_{17}O_2N_4ClNi$: N, 12.41; Cl, 7.85; Ni, 13.00. Found: N, 12.46; Cl, 7.97; Ni, 13.09; (Ni:Cl = 1:1).

Nickel *o*-Aminobenzaldehyde *o*-Aminobenzal-*m*-nitrobenzhydrazide.—A mixture of 0.25 g. of *o*-aminobenzaldehyde in 5 ml. of alcohol, 0.8 g. of *m*-nitrobenzhydrazide in 10 ml. of alcohol and 0.5 g. of nickel acetate in 5 ml. of water was warmed on a water-bath under reflux. The precipitate was recrystallized from dioxane and alcohol to give deep red needles which melted with decomposition at 232–233°.

Anal. Calcd. for $C_{21}H_{17}O_4N_5Ni$: N, 15.16; Ni, 12.70. Found: N, 15.65; Ni, 13.00.

Magnetic Measurements.—Susceptibility measurements were made with the modified Bhatnagar balance described previously.[6] The results are given in Table II; *n* is the number of unpaired electrons.

TABLE II

Nickel hydrazide	*t*, °C.	χ_g	χ_{mol}	χ_A	μ_{eff}	*n*
Bis-salicylidene-*p*-phenylbenzoyl	20	5.70	3928	4289	3.18	2
Bis-salicylidenehexahydrobenzoyl	20	7.52	4130	4419	3.23	2
Bis-salicylidenefuryl	20	7.44	3848	4078	3.10	2
Bis-salicylidene-3-methyl-5-isoxazolyl	20	6.40	3501	3747	2.97	2
Bis-salicylidene-α-naphthoyl	20	5.80	3695	4031	3.08	2
All of the bicyclic complexes II and V			Diamagnetic		0	0

Acknowledgment.—The financial assistance of the Italian National Research Council (C.N.R.), which supported this research, is gratefully acknowledged.

FLORENCE, ITALY

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[6] L. Sacconi, *Rend. Accad. Lincei*, [8] **VI**, 639 (1949); S. Bhatnagar and R. Mathur, *Phil. Mag.*, **8**, 1041 (1929); S. Bhatnagar, R. Mathur and Neogi, *Z. Physik*, **69**, 373 (1931).