the silver ion in this complex was coördinated mainly at the vinyl side chain rather than with the ring.

Although phenanthrene forms a more stable silver ion complex than does benzene, the K_c values for the iodine complexes of these aromatics are the same. It is possible that the phenanthrene-iodine results are somewhat in error as spectrophotometer readings, in this case, were made at high slit width settings, a procedure which is undesirable where high precision is required.

DAVIS, CALIFORNIA

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

Chemical Reactions of Complexes. I. Action of Hydrazides on Nickel Disalicylaldehyde

BY LUIGI SACCONI

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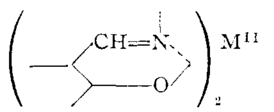
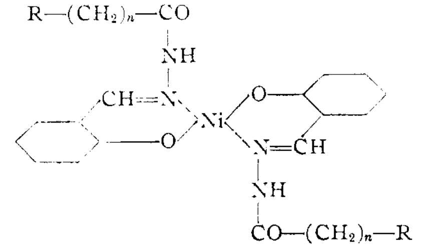
The reaction of hydrazides of the type $H_2N-NH-CO-R$ with nickel disalicylaldehyde (or with nickel acetate and salicylaldehyde) is dependent on the nature of the R group. If R = alkyl or arylalkyl, symmetrical paramagnetic ionic compounds are formed. If R = Ph or substituted Ph, bicyclic planar complexes are formed.

Starting with the first syntheses of Pfeiffer and co-workers,[1] many complexes of metal *o*-oxyazomethines have been described.

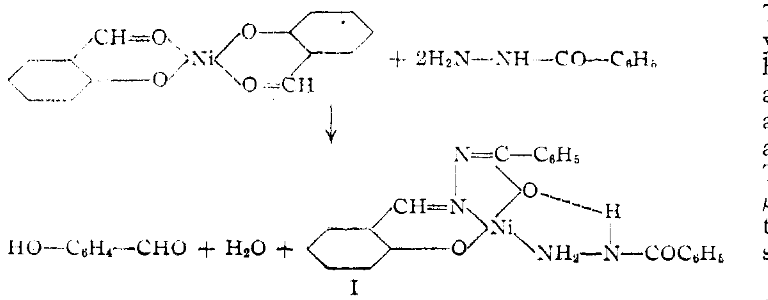


On treating nickel disalicylaldehyde with hydrazides of the type $H_2N-NH-CO-(CH_2)_n-R$, where R represents methyl or phenyl groups, nickel bissalicylidenehydrazides of the following structure are formed



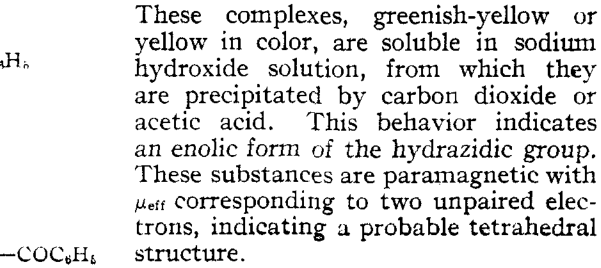
These complexes, green in color, are paramagnetic with a moment of about 3.3 Bohr magnetons. They therefore have four ionic sp^3 bonds and a tetrahedral configuration.

If R = phenyl and n = 0, two series of compounds are obtained. Initially formed are bicyclic complexes containing a tridentate group produced by a molecule of salicylidenebenzoylhydrazine reacting in enolic form, as represented by the reactions shown. These complexes, orange to red in color, are insoluble and stable in concentrated aqueous alkalies. They are diamagnetic and therefore have a planar arrangement of dsp^2 covalent bonds. The H---O bond in formula I accounts for the stability of the four planar bonds as well as the stability toward alkalies. The formation of bicyclic complexes when R = phenyl and n = 0 is undoubtedly due to the greater enolizing influence of the C_6H_5–CO– group, compared with that of the alkyl –CO– and the phenylalkyl –CO– groups.[2]



I

The bicyclic complexes are slowly transformed into symmetrical complexes by reaction with salicylaldehyde, either liberated from nickel disalicylaldehyde or added as such. This type of reaction can be represented by



II

These complexes, greenish-yellow or yellow in color, are soluble in sodium hydroxide solution, from which they are precipitated by carbon dioxide or acetic acid. This behavior indicates an enolic form of the hydrazidic group. These substances are paramagnetic with μ_{eff} corresponding to two unpaired electrons, indicating a probable tetrahedral structure.

o-Aminobenzoylhydrazine is an exception, however, since the following asymmetrical paramagnetic complex is first formed

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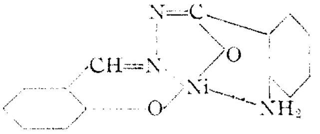
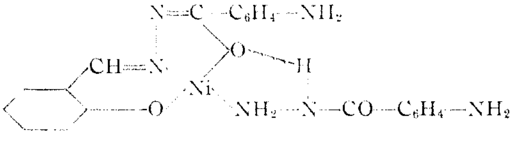
[1] P. Pfeiffer and co-workers, *J. prakt. Chem.*, **129**, 163 (1931); **145**, 243 (1936); **150**, 261 (1938); *Ann.*, **503**, 84 (1933); *Angew. Chem.*, **62**, 201 (1950); L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 2000 (1937).

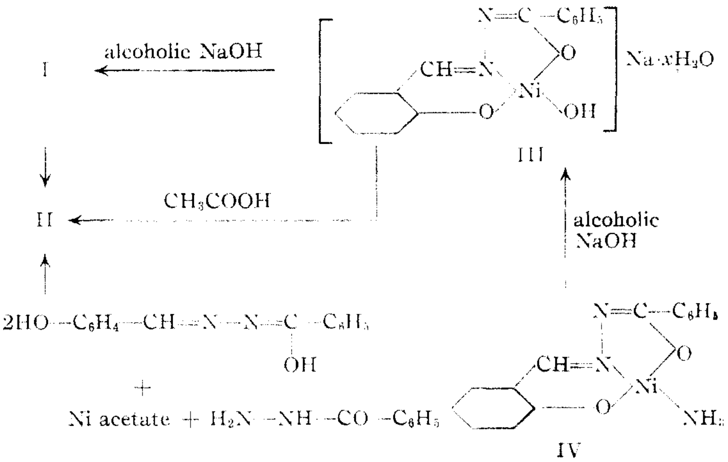
[2] R. A. Morton, A. Hassan and T. C. Calloway, *ibid.*, **883** (1934).



Because of strain, the complex is ionic and probably tetrahedral, as shown by the value of μ_{eff} = 3.0. This compound, treated with *o*-aminobenzoylhydrazine, yields the corresponding diamagnetic bicyclic complex



On treating the bicyclic complex I with alcoholic sodium hydroxide, a red solution results. From this solution a substance precipitates in which the ratio of Ni to N is 1:2 and which can be considered as the sodium salt of nickelo-salicylidenebenzoylhydrazine hydroxide (III). The same complex is formed when the complex nickel amine-salicylidenebenzoylhydrazide which is formed from nickel acetate and salicylidenebenzoylhydrazine in ammonia solution is treated with alcoholic sodium hydroxide. To this complex, which is diamagnetic and therefore planar with respect to the four dsp^2 covalent bonds, the formula IV must be assigned.



Bicyclic complexes of type I cannot be prepared from nickel acetate, salicylidenebenzoylhydrazine and a hydrazide. Instead, type II complexes are formed since the hydrazide does not take part in the reaction. These symmetrical complexes are also formed by the action of acetic acid on the hydroxocomplex III.

The bicyclic complexes melt with decomposition more than 30° below the decomposition temperatures of the corresponding symmetrical complexes. This is additional evidence of the covalent character of the bonds in the bicyclic type of complex.

Schiff's bases of the symmetrical complexes are formed when *m*- and *p*-aminobenzoylhydrazine are used. Pure samples of these compounds have not, however, been obtained and they are not reported in detail.

5-Chloro- and 5-bromosalicylaldehyde give symmetrical but not bicyclic complexes with benzhydrazide and nickel ion.

Experimental

All of the complexes herein reported are very sparingly soluble in alcohol, ether, chloroform and benzene.

Preparation of Complexes with H_2N-NH-CO-$(CH_2)_n$-R.—Two general methods of preparation were used. *First method:* Nickel disalicylaldehyde was suspended in a solution of the hydrazide in alcohol (50–100 ml. of alcohol per one gram of nickel disalicylaldehyde). The ratio of reactants was 2.2 moles of hydrazide to one mole of nickel disalicylaldehyde. *Second method:* A solution of the hydrazide in alcohol was added to a water solution of nickel acetate (one gram in 10 ml.) and the salicylaldehyde. The ratio of reactants was 2 moles of hydrazide to one mole of nickel acetate to 2 moles of salicylaldehyde. In both cases the mixture was heated on the water-bath under reflux, giving a solution from which the complex precipitated. After cooling, the complex was filtered, washed with alcohol and ether, and dried over phosphoric oxide in a vacuum desiccator. The dried samples were usually pure enough for analysis.

Nickel Bis-salicylidenebutyrylhydrazide.—Light green microcrystalline powder which does not melt at 350°. *Anal.* Calcd. for $C_{22}H_{26}O_4N_4Ni$: N, 11.94; Ni, 12.51. Found: N, 11.68; Ni, 12.02.

Nickel Bis-salicylidenecapronylhydrazide.—Light green microcrystalline powder which does not melt at 350°. *Anal.* Calcd. for $C_{26}H_{34}O_4N_4Ni$: N, 10.67; Ni, 11.17. Found: N, 10.88; Ni, 11.08.

Nickel Bis-salicylidenelaurylhydrazide.—Light green microcrystalline powder which decomposes above 325°. *Anal.* Calcd. for $C_{38}H_{58}O_4N_4Ni$: N, 8.08; Ni, 8.46. Found: N, 8.21; Ni, 8.58.

Nickel Bis-salicylidenemyristylhydrazide.—Light greenish powder which decomposes above 315°. *Anal.* Calcd. for $C_{42}H_{66}O_4N_4Ni$: N, 7.47; Ni, 7.83. Found: N, 7.63; Ni, 8.05.

Nickel Bis-salicylidenephenylacetylhydrazide.—Light green powder which decomposes at 330°. *Anal.* Calcd. for $C_{30}H_{26}O_4N_4Ni$: N, 9.91; Ni, 10.38. Found: N, 9.90; Ni, 10.38.

Nickel Bis-salicylidenephenylpropionylhydrazide.—Light green microcrystalline powder which decomposes above 300°. *Anal.* Calcd. for $C_{32}H_{30}O_4N_4Ni$: N, 9.44; Ni, 9.89. Found: N, 9.53; Ni, 9.80.

Preparation of Bicyclic Complexes with H_2N-NH-CO-R.—In these preparations R is an aryl group. It is usually better to use nickel disalicylaldehyde rather than nickel acetate. The first method of preparation was used, but without reflux. The complex which precipitated from the brown or red solution was rapidly filtered. Any symmetrical complex which formed concurrently was removed by warming the mixture with 4% sodium hydroxide, filtering and washing the residue with water, alcohol and ether.

Nickel Benzoylhydrazine Salicylidenebenzoylhydrazide.—Red-orange crystalline powder, melting at 255–257° with decomposition. *Anal.* Calcd. for $C_{21}H_{18}O_3N_4Ni$: N, 12.94; Ni, 13.55. Found: N, 12.90; Ni, 13.72.

Nickel *m*-Chlorobenzoylhydrazine Salicylidene-*m*-chlorobenzoylhydrazide.—Orange crystalline powder as small plates, melting at 250–251° with decomposition. *Anal.* Calcd. for $C_{21}H_{16}O_3N_4Cl_2Ni$: N, 10.93; Ni, 11.45; Cl, 14.16. Found: N, 11.02; Ni, 11.78; Cl, 14.24.

Nickel *p*-Chlorobenzoylhydrazine Salicylidene-*p*-chlorobenzoylhydrazide.—Orange-salmon microcrystalline powder as very small needles, decomposing above 170°. *Anal.* Calcd. for $C_{21}H_{16}O_3N_4Cl_2Ni$: N, 10.93; Ni, 11.45; Cl, 14.16. Found: N, 10.93; Ni, 11.65; Cl, 14.18.

Nickel *m*-Nitrobenzoylhydrazine Salicylidene-*m*-nitrobenzoylhydrazide.—Orange crystalline powder as needles and rhombic plates, melting at 259–261° with decomposition. *Anal.* Calcd. for $C_{21}H_{16}O_7N_6Ni$: N, 16.07; Ni, 11.22. Found: N, 16.17; Ni, 11.20.

Nickel *p*-Nitrobenzoylhydrazine Salicylidene-*p*-nitrobenzoylhydrazide.—One gram of nickel acetate in 8 ml. of water was mixed on the water-bath with 0.40 g. of salicylaldehyde and 1.76 g. of the hydrazide in 80 ml. of alcohol, giving a red microcrystalline powder which decomposes at 280°. *Anal.* Calcd. for $C_{21}H_{16}O_7N_6Ni$: N, 16.07; Ni, 11.22. Found: N, 16.12; Ni, 11.51.

Preparation of Symmetrical Complexes with H_2N–NH–CO–R.—In these preparations R is an aryl group. Either general method may be used. Treatment on the water-bath under reflux is necessary in order to transform the bicyclic complexes into the symmetrical complexes. It is advisable to use 2 ml. of salicylaldehyde in excess for each gram of nickel disalicylaldehyde or nickel acetate used.

Nickel Bis-salicylidenebenzoylhydrazide.—Yellow crystalline powder as rhombic plates, decomposing at 285–290°. *Anal.* Calcd. for $C_{28}H_{22}O_4N_4Ni$: N, 10.43; Ni, 10.92. Found: N, 10.63; Ni, 10.88.

Nickel Bis-salicylidene-*o*-chlorobenzoylhydrazide.—Greenish-yellow microcrystalline powder, melting at 295–300° with decomposition. *Anal.* Calcd. for $C_{28}H_{20}O_4N_4Cl_2Ni$: N, 9.24; Cl, 11.70; Ni, 9.68. Found: N, 8.94; Cl, 11.61; Ni, 9.62.

Nickel Bis-salicylidene-*m*-chlorobenzoylhydrazide. Greenish-yellow microcrystalline powder, melting at 315–320° with decomposition. *Anal.* Calcd. for $C_{28}H_{20}O_4N_4Cl_2Ni$: N, 9.24; Cl, 11.70; Ni, 9.68. Found: N, 8.98; Cl, 11.77; Ni, 9.62.

Nickel Bis-salicylidene-*p*-chlorobenzoylhydrazide.—Greenish-yellow microcrystalline powder which does not melt at 350°. *Anal.* Calcd. for $C_{28}H_{20}O_4N_4Cl_2Ni$: N, 9.24; Cl, 11.70; Ni, 9.68. Found: N, 9.27; Cl, 11.83; Ni, 9.46.

Nickel Bis-salicylidene-*m*-nitrobenzoylhydrazide.—Greenish-yellow microcrystalline powder which does not melt at 330°. *Anal.* Calcd. for $C_{28}H_{20}O_8N_6Ni$: N, 13.40; Ni, 9.36. Found: N, 13.19; Ni, 9.43.

Nickel Bis-salicylidene-*p*-nitrobenzoylhydrazide.—This compound was obtained by treating the corresponding bicyclic complex, suspended in alcohol with a great excess of salicylaldehyde, on the water-bath under reflux for several hours. Orange-brown microcrystalline powder which does not melt at 335°. *Anal.* Calcd. for $C_{28}H_{20}O_8N_6Ni$: N, 13.40; Ni, 9.36. Found: N, 13.36; Ni, 9.37.

Nickel Bis-salicylidene-*p*-aminobenzoylhydrazide.—Better prepared by the second method. Greenish-yellow powder which does not melt at 350°. *Anal.* Calcd. for $C_{28}H_{24}O_4N_6Ni$: N, 14.82; Ni, 10.35. Found: N, 14.59; Ni, 10.38.

Nickel Salicylidene-*o*-aminobenzoylhydrazide.—One gram of nickel acetate in 10 ml. of water was mixed with 0.6 g. of *o*-aminobenzoylhydrazine in 25 ml. of alcohol and 0.5 g. of salicylaldehyde. On the water-bath under reflux the compound precipitated as a yellow microcrystalline powder which does not melt at 350°. *Anal.* Calcd. for $C_{14}H_{12}O_2N_3Ni$: N, 13.43; Ni, 18.75. Found: N, 13.62; Ni, 18.92.

Nickel *o*-Aminobenzoylhydrazine Salicylidene-*o*-aminobenzoylhydrazide.—The preceding compound was suspended in an alcoholic solution of *o*-aminobenzoylhydrazine and boiled on the water-bath under reflux. Orange-salmon microcrystalline powder, as small needles. *Anal.* Calcd. for $C_{21}H_{20}O_3N_6Ni$: N, 18.15; Ni, 12.66. Found: N, 18.13; Ni, 12.64.

Nickel Bis-5-chlorosalicylidenebenzoylhydrazide.—Prepared by refluxing on the water-bath a mixture of a 10% water solution of nickel acetate, a 5% alcohol solution of benzoylhydrazine, and a 3% alcohol solution of 5-chlorosalicylaldehyde. The reagents were in the mole ratio of 1:2:2, as listed. The product is a greenish-yellow powder which does not melt at 330°. *Anal.* Calcd. for $C_{28}H_{20}O_4N_4Cl_2Ni$: N, 9.24; Ni, 9.68. Found: N, 9.16; Ni, 10.13.

Nickel Bis-5-bromosalicylidenebenzoylhydrazide was prepared as in the preceding case. Greenish-yellow powder which does not melt at 350°. *Anal.* Calcd. for $C_{28}H_{20}O_4N_4Br_2Ni$: N, 8.06; Ni, 8.44. Found: N, 7.98; Ni, 8.19.

Nickel Amine Salicylidenebenzoylhydrazide.—0.5 g. of salicylidenebenzoylhydrazine, dissolved in 35 ml. of concentrated ammonia, was mixed with 0.5 g. of nickel acetate in 5 ml. of concentrated ammonia. The solution was warmed on the water-bath. The red orange solid which precipitated after 15–30 minutes was filtered and washed with water. *Anal.* Calcd. for $C_{14}H_{13}O_2N_3Ni$: N, 13.39; Ni, 18.70. Found: N, 13.37; Ni, 18.83.

Magnetic Measurements.—Susceptibility measurements were made by means of the modified Bhatnagar balance previously described.[3] The results are given in Table I. The values of X_A are obtained from X_{mol} by use of Pascal's constants,[4] the values of μ_{eff} in Bohr magnetons are calculated from $\mu_{eff} = 2.84\sqrt{X_A \cdot T}$, while n is the number of unpaired electrons calculated from the familiar "spin only" formula.

TABLE I

Nickel hydrazide	t, °C.	X_g	X_{mol}	X_A	μ_{ef}	n
Bis-salicylidenebutyryl	25.1	8.85	4122	4341	3.0	2
Bis-salicylidenecapronyl	25.1	8.97	4710	4976	3.4	2
Bis-salicylidenelauryl	25.1	6.50	4506	4856	3.4	2
Bis-salicylidenemyristyl	25.1	5.64	4229	4663	3.3	2
Bis-salicylidenephenylacetyl	26.3	7.45	4211	4481	3.2	2
Bis-salicylidenephenylpropionyl	26.3	6.72	3986	4282	3.2	2
Bis-salicylidenebenzoyl	25.1	6.70	3599	3850	3.0	2
Bis-salicylidene-*o*-chlorobenzoyl	25.1	6.75	4091	4376	3.2	2
Bis-salicylidene-*m*-chlorobenzoyl	25.1	6.24	3782	4067	3.1	2
Bis-salicylidene-*p* chlorobenzoyl	25.1	6.92	4194	4479	3.3	2
Bis-salicylidene-*m*-nitrobenzoyl	25.1	5.80	3639	3895	3.1	2
Bis-salicylidene-*p*-nitrobenzoyl	25.1	6.12	3838	4094	3.2	2
Salicylidene-*o*-aminobenzoyl	24.9	11.4	3507	3656	3.0	2
Bis-salicylidene-*p*-aminobenzoyl	25.1	7.06	4004	4272	3.2	2
Bis-5-chlorosalicylidenebenzoyl	24.9	6.85	4155	4440	3.2	2
Bis-5-bromosalicylidenebenzoyl	24.9	5.94	4130	4436	3.2	2
Benzoylhydrazine salicylidenebenzoyl and other bicyclic complexes		Diamagnetic			0	0
Amino salicylidenebenzoyl		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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[3] 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).

[4] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1945, p. 51.