

cell, may play some role also in the phenomenon considered here.

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PALERMO, ITALY

[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO]

## Studies in Coördination Chemistry. II. Spectrophotometric Investigation of Some Hydrazidic Tetracovalent Nickel(II) Complexes

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The ultraviolet absorption spectra of a number of hydrazidic tetracovalent nickel(II) complexes have been measured. The effect of certain atomic grouping adjacent to the chelate ring has been studied and discussed in terms of the hypothesis of dative  $\pi$ -bond in metal complexes.

The concept of double bond formation between metals and donor atoms is now regarded as of great importance in many complexes.<sup>1</sup>

Pauling was the first to explain the unusual strength and shortening of some metal-ligand bonds in certain coördination compounds by the hypothesis of double bonding.<sup>2</sup> In the case of nickel complexes it was suggested that the formation of double bond using  $d_{\pi}$  electron pairs of the metal and a vacant p or d orbital of the donor atom is an important factor influencing the formation of the square arrangement.<sup>3</sup>

With the aim to collect new experimental observations on the problem of dative  $\pi$ -bonding in metal complexes,<sup>4</sup> spectrophotometric measurements have been carried out on two groups of hydrazidic nickel(II) complexes in which two six-membered rings, the chelate and the aromatic one, are present. In compounds of the type I, namely, nickel complexes with acylhydrazones of *o*-oxyaldehydes and ketones, the rings are condensed; in those of the type II, namely, nickel complexes with acylhydrazones of benzoylacetone, the rings are joined by a C-C bond.

All of these complexes, from orange to red in color are diamagnetic, therefore planar with respect to the four  $d_{sp^2}$  covalent bonds. One of the coördinative valences of the nickel central atom is saturated by ammonia, ethylamine or triethylphosphine.

### Experimental

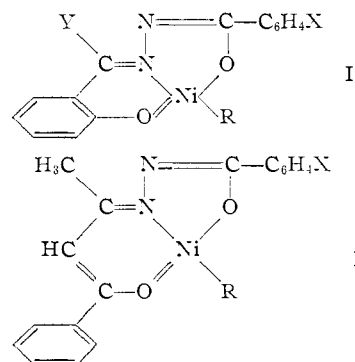
**Preparation of Compounds.**—Salicylidenebenzoylhydrazonenickel(II)-ammine, salicylidene-*p*-chlorobenzoylhydrazonenickel(II)-ammine, *o*-oxyacetophenonebenzoylhydrazonenickel(II)-ammine, benzoylacetonebenzoylhydrazonenickel(II)-ammine.

(1) R. S. Nyholm, *Rev. Pure Appl. Chem. (Australia)*, **4**, 15 (1954); A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 160; Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules," Butterworths Sci. Publ., London, 1950, p. 361.

(2) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 250.

(3) R. S. Nyholm, *Chem. Revs.*, **53**, 276 (1953).

(4) Cf. G. E. Coates, *J. Chem. Soc.*, 2003 (1951); J. Chatt and A. A. Williams, *ibid.*, 3061 (1951); J. Chatt and R. G. Wilkins, *ibid.*, 273, 4300 (1952); R. S. Nyholm and F. H. Burstall, *ibid.*, 3570, 3579 (1952); J. Chatt, L. A. Duncanson and L. M. Venanzi, *ibid.*, 4461 (1955); R. K. Murmann and F. Basolo, *THIS JOURNAL*, **77**, 3484 (1955).



Y = H, CH<sub>3</sub>; X = H, Cl; R = NH<sub>3</sub>, NH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

nickel(II)-ammine and benzoylacetone-*p*-chlorobenzoylhydrazonenickel(II)-ammine complexes were prepared as previously described.<sup>5</sup>

***o*-Oxyacetophenone-*p*-chlorobenzoylhydrazone.**—*p*-Chlorobenzoylhydrazide (1.3 g.) in 8 ml. of alcohol and *o*-oxyacetophenone (1.1 g.) in 3 ml. of alcohol were refluxed over a water-bath for few minutes; water was then added in order to obtain a crystalline precipitate melting at 223–225°.

*Anal.* Calcd. for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>Cl: N, 9.70. Found: N, 9.68.

***o*-Oxyacetophenone-*p*-chlorobenzoylhydrazonenickel(II)-ammine.**—A mixture of 0.9 g. of nickel(II) acetate in 10 ml. of concd. ammonia and 1 g. of *o*-oxyacetophenone-*p*-chlorobenzoylhydrazone suspended in 15 ml. of alcohol was heated on a water-bath. Orange needles which do not melt at 270° were obtained.

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>N<sub>3</sub>ClNi: N, 11.59; Ni, 16.19. Found: N, 11.63; Ni, 16.10.

**Salicylidenebenzoylhydrazonenickel(II)-ethylamine.**—A mixture of 1 g. of nickel(II) acetate in 16 ml. of 50% alcohol and 8 ml. of 33% ethylamine and 0.66 g. of salicylidenebenzoylhydrazone in 30 ml. of alcohol was warmed on a water-bath to obtain red needles of m.p. 132° dec.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub>Ni: N, 12.28; Ni, 17.16. Found: N, 12.19; Ni, 17.17.

**Salicylidenebenzoylhydrazonenickel(II)-triethylphosphine.**—Nickel(II) acetate (1 g.) in 16 ml. of 50% alcohol and 1 g. of triethylphosphine was mixed with 0.66 g. of salicylidenebenzoylhydrazone in 30 ml. of alcohol. The mixture was warmed on a water-bath under reflux. Orange tablets of m.p. 105–106° dec. were obtained.

*Anal.* Calcd. for C<sub>20</sub>H<sub>25</sub>O<sub>2</sub>N<sub>2</sub>PNi: N, 6.75; P, 7.47; Ni, 14.14. Found: N, 6.97; P, 8.05; Ni, 14.40.

***o*-Oxyacetophenonebenzoylhydrazonenickel(II)-ethyl-**

(5) L. Sacconi, *Gazz. chim. ital.*, **83**, 884 (1953); *Z. anorg. allgem. Chem.*, **275**, 249 (1954); *THIS JOURNAL*, **75**, 5434 (1953).

amine.—Nickel(II) acetate (1 g.) in 20 ml. of alcohol and 10 ml. of 33% ethylamine was mixed with 1 g. of *o*-oxyaceto-

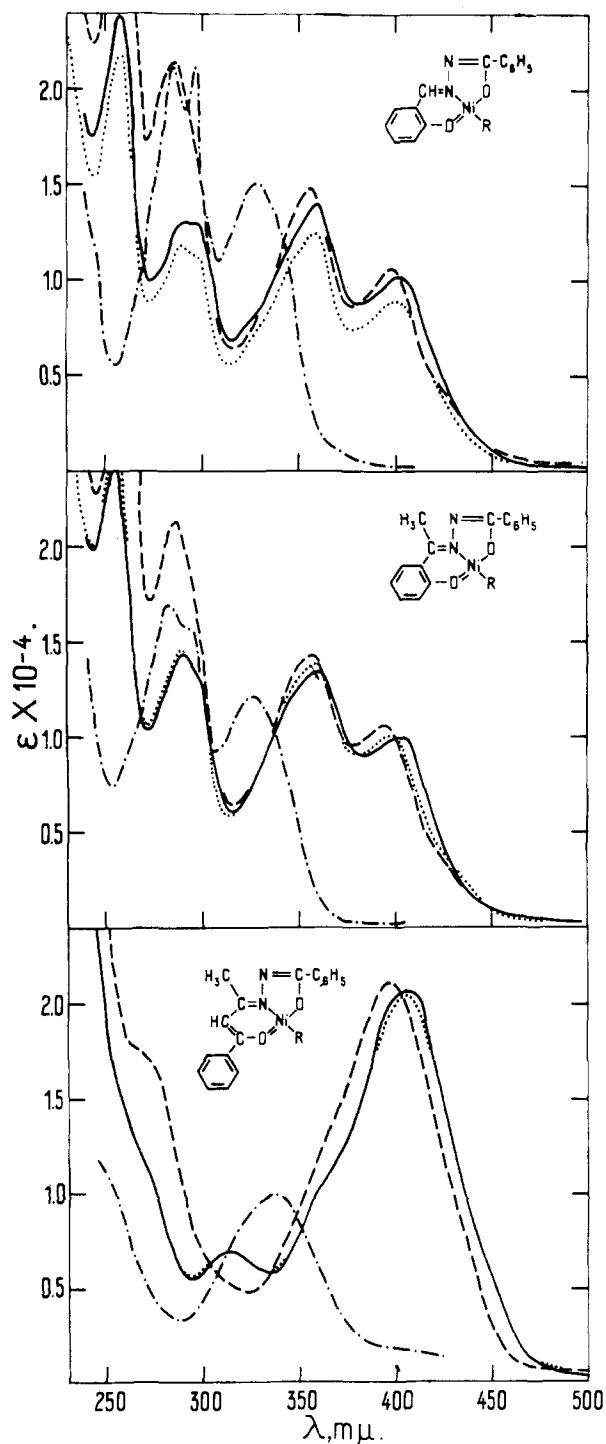


Fig. 1.—Absorption spectra of the ligands with X = H (— · — · —) and related complexes with R = NH<sub>3</sub> (—), R = NH<sub>2</sub>C<sub>2</sub>H<sub>5</sub> (· · · · ·) and R = P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (— · — · —).

phenonebenzoylhydrazone in 30 ml. of alcohol. The mixture was heated on a water-bath for few minutes to yield red prisms of m.p. 141–142° dec.

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub>Ni: N, 11.80; Ni, 14.49. Found: N, 11.84; Ni, 14.43.

*o*-Oxyacetophenonebenzoylhydrazonenickel(II)-triethylphosphine.—A solution of 1 g. of nickel(II) acetate in 6 ml. of water, 12 ml. of alcohol and 1 g. of triethylphosphine was mixed with 1 g. of *o*-oxyacetophenonebenzoylhydrazone suspended in 30 ml. of alcohol. The mixture was warmed on a water-bath under reflux for a few minutes. Orange-red prisms were obtained which melt, with decomposition, at 98–99°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>27</sub>O<sub>2</sub>N<sub>2</sub>PNi: N, 6.55; P, 7.22; Ni, 13.68. Found: N, 6.71; P, 7.65; Ni, 13.63.

Benzoylacetonebenzoylhydrazonenickel(II)-ethylamine.—A mixture of 1 g. of nickel(II) acetate in 20 ml. of water and 10 ml. of 33% ethylamine and 1.1 g. of benzoylacetonebenzoylhydrazone in 20 ml. of alcohol was warmed on a water-bath under reflux for few minutes. Addition of water facilitates the formation of red-orange needles of m.p. 130–131° dec.

*Anal.* Calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N<sub>2</sub>Ni: N, 11.00; Ni, 15.36. Found: N, 11.40; Ni, 15.43.

Benzoylacetonebenzoylhydrazonenickel(II)-triethylphosphine.—A mixture of 1 g. of nickel(II) acetate in 20 ml. of alcohol and 1 g. of triethylphosphine and 1.1 g. of benzoylacetonebenzoylhydrazone in 40 ml. of alcohol was warmed on a water-bath under reflux for few minutes. On standing at 0–5° red crystals separated which melt with decomposition at 101–102°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>29</sub>O<sub>2</sub>N<sub>2</sub>PNi: N, 6.15; P, 6.81; Ni, 12.89. Found: N, 6.37; P, 6.79; Ni, 12.85.

All the complexes are soluble in alcohol, ether, benzene, chloroform. Those with triethylphosphine are also soluble in petroleum ether.

**Spectra of Ligands and Complexes.**—Spectrophotometric measurements were made with a Beckman DU spectrophotometer using silica cells 1 cm. long, on alcohol solutions of chelating agents and nickel complexes of 8.5 × 10<sup>-5</sup> M concentration.

## Results

Spectral data for acylhydrazones and complexes are recorded in Table I, where  $\epsilon$  signifies molecular extinction coefficient.

TABLE I  
ABSORPTION CHARACTERISTIC OF LIGANDS AND COMPLEXES

	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max}$ × 10 <sup>-4</sup>
Type I		
<i>o</i> -Oxyacetophenonebenzoylhydrazone	326	1.23
<i>o</i> -Oxyacetophenone- <i>p</i> -chlorobenzoylhydrazone	328	1.36
Salicylidenebenzoylhydrazone	328	1.51
Salicylidene- <i>p</i> -chlorobenzoylhydrazone	330	1.66
Type II		
Benzoylacetonebenzoylhydrazone	335	1.01
Benzoylacetone- <i>p</i> -chlorobenzoylhydrazone	336	1.25
Type I		
<i>o</i> -Oxyacetophenone-benzoylhydrazone-Ni-NH <sub>3</sub>	400	0.97
<i>o</i> -Oxyacetophenone- <i>p</i> -chlorobenzoylhydrazone-Ni-NH <sub>3</sub>	402	1.12
<i>o</i> -Oxyacetophenonebenzoylhydrazone-Ni-NH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	398	1.01
<i>o</i> -Oxyacetophenonebenzoylhydrazone-Ni-P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	394	1.07
Salicylidenebenzoylhydrazone-Ni-NH <sub>3</sub>	402	1.02
Salicylidene- <i>p</i> -chlorobenzoylhydrazone-Ni-NH <sub>3</sub>	404	1.16
Salicylidenebenzoylhydrazone-Ni-NH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	400	0.90
Salicylidenebenzoylhydrazone-Ni-P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	396	2.11
Type II		
Benzoylacetonebenzoylhydrazone-Ni-NH <sub>3</sub>	405	2.10
Benzoylacetone- <i>p</i> -chlorobenzoylhydrazone-Ni-NH <sub>3</sub>	409	2.39
Benzoylacetonebenzoylhydrazone-Ni-NH <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	404	2.03
Benzoylacetonebenzoylhydrazone-Ni-P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	396	2.11

Experimental absorption curves for compounds with X = H are shown in Fig. 1. Compounds with X = Cl exhibit analogous features.

## Discussion

The spectra obtained for the ligands of the type I show two bands in the 280–290 and 326–336 m $\mu$

regions. The latter maximum could be considered as the 325  $m\mu$  band of the salicylaldehyde<sup>6</sup> shifted toward longer wave lengths owing to the formation of the benzoylhydrazone. This band can be ascribed to the existence of a chelate enol ring stabilized through hydrogen-bond formation and enol resonance.<sup>7</sup>

Beside showing a very strong absorption band in the ultraviolet region below 250  $m\mu$ , the spectra of the ligand molecules of type II show a maximum at 336  $m\mu$ . This band presumably can be related to the band at 310  $m\mu$  ascribed to the enol form of benzoylacetone.<sup>6</sup>

The spectra of the complexes of type I show four absorption bands at *ca.* 260, *ca.* 280, *ca.* 360 and 400–410  $m\mu$ . The band at *ca.* 410  $m\mu$  may be identified as the characteristic band of covalent nickel chelates, which is due to the presence of a chelate ring of which the metal is a member.<sup>8</sup> The intensity of this band (of  $\epsilon \approx 10^4$ ) is that of an allowed transition.<sup>9</sup>

The main features of the absorption spectra of type II complexes consist of two absorption bands in the 340 and 400–410  $m\mu$  regions. The former, of smaller intensity, is lacking in the complex with triethylphosphine. The band at 406–410  $m\mu$  can be recognized as that of the Ni chelates with *dsp*<sup>2</sup> covalent structure.

Table I shows that the molecular extinction coefficient of the nickel band maximum at 400–410  $m\mu$  increases from the values 9,000–11,600 for the complexes of the type I, to values 21,100–23,900 for the complexes of the type II. Hence the position of the aromatic nucleus, adjacent to the

chelate ring in the complexes of type I, attached by a C–C bond in the complexes of type II, influences the chromophoric grouping responsible for this band, *i.e.*, the chelate ring containing the nickel atom. This fact can be related to the existence in the chelate ring of the complexes of a completely conjugated resonance which interferes with the resonance of the aromatic nucleus when the two rings are condensed. Thus a "crossed resonance" of the type already studied for some copper chelates<sup>10</sup> is produced. This "cross conjugation"<sup>11</sup> implies the participation of a nickel atom in the  $\pi$ -bond system of the coördinate ring.

The absence of an hyperchromic effect in the maxima at 326–336  $m\mu$  of the spectra of ligands of type II can be explained keeping in mind that the chromophore possibly responsible for such maxima is not a completely conjugated system. In fact it is obvious that the hydrogen atom which completes the enol ring in the ligand molecules is incapable of forming double bonds.

These results therefore are consistent with the concept of  $\pi$ -bond character of the coördinate links between nickel and donor atoms in the above complexes.

The hyperchromic and bathochromic effects caused by the presence of a chlorine atom in the molecules of both ligands and complexes must be noticed. The substitution of ethylamine and triethylphosphine for ammonia produces only a little hypsochromic shift of the band at about 400  $m\mu$ . This fact is in accordance with the assumption that this band is due to the presence of a chelate ring including the nickel atom.

**Acknowledgment.**—We are indebted to the Italian "Consiglio Nazionale delle Ricerche" (C.N.R.) for the financial support of this work.

(10) M. Calvin and R. H. Bailes, *THIS JOURNAL*, **68**, 949 (1946); *cf.* A. E. Martell and M. Calvin, *ref. 1*, p. 164.

(11) L. N. Ferguson, *ref. 7*, p. 43.

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(6) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Publishers, Ltd., London, 1954, pp. 128, 223.

(7) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 216.

(8) *Cf.* H. A. McKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Roy. Soc. N.S. Wales*, **78**, 70 (1944); A. E. Martell and M. Calvin, *ref. 1*; K. Sone, *THIS JOURNAL*, **75**, 5207 (1953).

(9) *Cf.* R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

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## The Gluconate Complexes. IV. The Cadmium-Gluconate System

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Cadmium in varying concentrations of gluconate has been investigated polarographically from *pH* 2 to 14. A number of complexes are formed. Those which were identified and studied have a ratio of cadmium to gluconate of 1:2 (*pH* 5 to 8), 2:3 (*pH* 13 to 14), and 2:1 (*pH* 13 to 14). Half-wave potentials and dissociation constants are given.

Although it is known that gluconic acid forms complexes with many metal ions, no previous description of the cadmium-gluconate system is available. The complexes do not give spectra suitable for study, therefore this investigation is entirely polarographic. As in most supporting electrolytes, cadmium in gluconate solutions gives well-defined, reversible polarograms which are subject to thermodynamic interpretation.

### Experimental

The polarographic equipment and methods used have been described previously.<sup>1</sup> The purification and preparation of solutions of gluconic acid and sodium gluconate also have been described.<sup>1</sup> A stock solution of cadmium perchlorate was prepared by dissolving cadmium hydroxide in perchloric acid and standardized electrolytically. Conductivity water was used throughout. The ionic strength was adjusted to

(1) R. L. Pecsok and R. S. Juvet, Jr., *THIS JOURNAL*, **77**, 202 (1955).