# HEATS OF FORMATION AND COÖRDINATE BOND ENERGIES OF SOME NICKEL(II) CHELATES

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Heats of formation of eight inner complex salts of nickel(II) have been determined using measurements of their heats of combustion in an oxygen bomb calorimeter. Heats of vaporization of these complexes and their constituent ligands have been determined from static vapor pressure measurements with an isoteniscope. From these, coördinate bond energies for the Ni–O and Ni–N bonds have been determined by the use of a thermochemical cycle. These bond energies are not strictly constant, but show a definite dependence upon the coordination environment.

Earlier work in this Laboratory<sup>1</sup> showed how coördinate bond energies in inner complex salts could be obtained from heats of combustion and heats of vaporization of these materials. The present study extends these measurements to eight nickel(II) complexes, most of which contain nickel(II) in a square planar coördination environment. The complexes reported upon here contain only Ni-O or Ni-N coördinate bonds. Some work with sulfur-containing ligands was carried out but was found to be attended with special difficulties (e.q.)the corrosion of the calorimeter and poorlyd efined combustion products). Concentration of effort on complexes containing only two kinds of coördinate bonds has the advantage that a reasonable estimate of the constancy of the bond energy can be made. Every effort was also exerted to utilize the structural information on these complexes so that the bond energy calculations are in accord with such data as are available.

#### Experimental

A Parr adiabatic calorimeter was used to determine the heats of combustion. The general procedure and the calibrations were carried out as described previously.<sup>1</sup>

The bis-(acetylacetonato)-nickel(II) used in this work was obtained from the MacKenzie Chemical Works, Central Islip, Long Island, N. Y. It was recrystallized from chloroform prior to use. Anal. Calcd. for  $Ni(C_5H_7O_2)_2$ : Ni, 22.85. Found: Ni, 22.69.

**Bis-(dimethylglyoximato)-nickel(II)** was prepared by the scaling up of a standard procedure.<sup>2</sup> The product was dried in an oven at 105° for 2.5 hours prior to use. The complex was analyzed for its nickel content by first destroying it with boiling sulfuric acid, then evaporating the resulting solution to dryness. The residue was taken up with water, the solution was rendered ammoniacal and the nickel was then electrolytically deposited on a platinum cathode. This method was used for all the remaining complexes except the complex with 8-hydroxyquinoline, which was analyzed by ignition to NiO.

Caled. for NiC8H4O4N4: Ni, 20.32. Found: Ni, 20.30.

Bis-(glyoximato)-nickel(II) was prepared by a direct precipitation. Reagent grade nickel chloride hexahydrate (40.8 g., 0.172 mole) was dissolved in water (100 ml.). A solution of glyoxime (32 g., 0.326 mole) in alcohol was slowly added to the nickel chloride solution. Powdered sodium bicarbonate was then added in small portions and the dark red complex precipitated as the solution became basic. The precipitate was filtered, washed with alcohol, and air dried; yield 36 g. (0.137 mole). Calcd. for NiC<sub>4</sub>H<sub>6</sub>N<sub>4</sub>O<sub>4</sub>: Ni, 25.22. Found: Ni, 25.10. Bis-(salicylaldehydato)-nickel(II).—Reagent grade nickel chlo-

**Bis-(salicylaldehydato)-nickel(II)**.—Reagent grade nickel chloride hexahydrate (23.7 g., 0.0997 mole) was dissolved in water, and redistilled salicylaldehyde (23.7 g., 0.194 mole) was added slowly and with constant stirring. Aqueous ammonia (30 ml. of 6 M) was then added and a greenish yellow precipitate was formed. After digesting the reaction mixture at 60° for one-half hour, the solution was filtered, the precipitate was washed with alcohol, and then dried in a vacuum oven at 110° for three hours: yield 24.7 g. (0.0821 mole). Calcd. for  $NiC_{14}H_{10}O_4$ : Ni, 19.51. Found: Ni, 19.69.

**Bis-(salicylaldiminato)-nickel(II)**.—Redistilled reagent grade salicylaldehyde (23.7 g., 0.194 mole) was dissolved in alcohol (100 ml.). This solution was added to a solution of nickel chloride hexahydrate (23.7 g., 0.0997 mole) in water (100 ml.) to which concentrated aqueous ammonia (39.6 ml.) had been added. A reddish orange precipitate formed immediately and was collected on a filter, washed with alcohol and air-dried; yield 28.2 g. (0.0943 mole). Calcd. for NiC<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: Ni, 19.64. Found: Ni, 19.30.

Bis-(8-quinolinato)-diaquonickel(II).—Nickel chloride hexahydrate (24.8 g., 0.104 mole) was dissolved in water (100 ml.) and concentrated aqueous ammonia solution (41.4 ml., 1.87 moles) was added. To this solution was added a solution of 8quinolinol (30.3 g., 0.209 mole) in alcohol (100 ml.). The yellow precipitate which formed was collected on a filter, washed with alcohol, and dried in a vacuum oven at 110° for two hours. Calcd. for NiC<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: Ni, 15.33, Found: Ni, 15.51.

**Bis-(picolinato)-nickel(II).**—A mixture of water (75 ml.) and aqueous ammonia (40 ml., 1.81 moles) was used to dissolve nickel chloride hexahydrate (32.9 g., 0.120 mole). Resublimed picolinic acid hydrochloride (44.4 g., 0.276 mole) dissolved in water (100 ml.) was added to this solution. The resulting blue solution was allowed to stir for one hour at 60° and was then filtered. Acctone (500 ml.) was added to the filtrate and a dark blue precipitate formed immediately. This precipitate was collected on a filter, washed with acetone, and then dried in a vacuum oven at 110° for eight hours. The final product was light blue; yield 29 g. (0.0957 mole). Calcd. for NiC<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>: Ni, 19.37. Found: Ni, 19.18.

TABLE	Ι
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#### Analyses of Solid Combustion Residues

Compound	% Ni found	Ni/NiO ratio
Bis-(acetylacetonato)-nickel(II)	77.62	All NiO
Bis-(dimethylglyoximato)-nickel(II)	Estimated	All NiO
Bis-(glyoximato)-nickel(II)	$\operatorname{Estimated}^{b}$	All Ni
Bis-(salicylaldehydato)-nickel(II)	78.21	All NiO
Bis-(salicyliminato)-nickel(II)	96.99	6:1
Bis-(8-quinolinato)-diaquonickel(II)	82.38	1:5
Bis-(picolinato)-nickel(II)	99.12	All Ni
Bis-(glycinato)-nickel(II)	Estimated <sup>b</sup>	All Ni

<sup>a</sup> Estimated from the color and particle size of the residue. <sup>b</sup> Estimated from the solid Ni present.

Bis-(glycinato)-nickel(II).—A slurry of reagent grade nickel(II) carbonate (11.87 g., 0.10 mole) in water (100 ml.) was prepared. A slight excess of ammonia-free reagent grade glycine (15.76 g., 0.21 mole) was added slowly while the solution was stirred and heated to 60°. The slurry disappeared and a dark blue solution was obtained. The solution was first filtered to remove any insoluble impurities and then treated with acetone (500 ml.). A light blue precipitate formed immediately and was collected on a filter, washed with acetone, and then dried in a vacuum oven at 110° for eight hours. The result was a light green anhydrous salt. Both of these solids are extremely soluble in water; yield of anhydrous compound, 20.0 g. (0.0966 mole). Caled. for NiC<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: Ni, 28.50. Found: Ni, 28.25.

The values of the heats of combustion for these compounds are the averages of a minimum of four separate determinations. The reproducibility varied somewhat from compound to com-

M. M. Jones, B. J. Yow, and W. R. May, Inorg. Chem., 1, 166 (1962).
 F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 176.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	mbustion ./mole 063.1 .48.1 .50.78 .17.8 .94.8 80.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	063.1 .48.1 50.78 .17.8 .94.8 .80.6
Bis-(dimethylglyoximato)-nickel(II) $288.94$ $-3973.4$ $-1148.1$ $0$ $-1138.1$ Bix-(glyoximato)-nickel(II) $232.83$ $-2372.0$ $-552.27$ $2.5$ $-480.25$ Bis-(salicylaldehydato)-nickel(II) $300.94$ $-5041.5$ $-1517.2$ $-1$ $-148.1$	$\begin{array}{c} 48.1 \\ 50.78 \\ 17.8 \\ 94.8 \\ 80.6 \end{array}$
Bix-(glyoximato)-nickel(II) $232.83$ $-2372.0$ $-552.27$ $2.5$ $-4$ Bis-(salicylaldehydato)-nickel(II) $300.94$ $-5041.5$ $-1517.2$ $-1$ $-14$	50.78 17.8 94.8 80.6
Bis-(salicylaldehydato)-nickel(II) 300.94 -5041.5 -1517.2 -1 -1	17.8 94.8 80.6
	94.8 80.6
Bis-(salicyliminato)-nickel(II) 298.98 -5332.0 -1594.2 -1.07 -14	80.6
Bis-(8-quinolinato)-diaquonickel(II) 383.07 -5950.7 -2279.5 -1.9 -22	
Bis-(picolinato)-nickel(II) $302.92$ $-4086.4$ $-1237.9$ $1$ $-1237.9$	37.3
Bis-(glycinato)-nickel(II) $206.83 - 2018.9 - 417.57 1 - 4$	16.97
8-Quinolinol $145.17 - 7351.6 - 1067.2 - 1067.2 - 1 - 1067.2$	67.8
Dimethylglyoxime $116.12 - 5255.0 - 610.21 - 1 - 60000000000000000000000000000000$	10.81
Picolinic acid $107.12 - 5297.4 - 567.46 - 1 - 567.46$	68.06
$\Delta H_{\mathrm{chel},(g)}$	
$Ni(g) + 2C_4H_7N_2O_2H(g) - H_2(g) \xrightarrow{\text{conv}(g)} Ni(C_4H_7N_2O_2)_2(g)$	
$2\Delta H_{2,vap}$ $-\Delta H_3$	
$Ni(C_4H_7N_2O_2)(s)$	
$\Delta H_{1,\mathrm{vap}}$ $2\mathrm{C}_4\mathrm{H}_7\mathrm{N}_2\mathrm{O}_2\mathrm{H}(\mathrm{s})$	
$\Delta H_{\rm e}$	
$2\Delta H_{\tilde{f},L}$ $\Delta H_{cr}$	
$Ni(s) + 8C(s) + 2N_2(g) + 13O_2(g) + 8H_2(g) - H_2(g)  NiO(s) + 8CO_2(g) + 7H_2O(1) + 2I_2O(1)$	T / 1

## TABLE II HEATS OF COMBUSTION

 $\Delta H_{\text{ox}} = \Delta H_{1,\text{vap}} + 2\Delta H_{f,1}^0 + 2\Delta H_{2,\text{vap}} + \Delta H_{\text{chel}(g)} - \Delta H_3 + \Delta H_c$  $\Delta H_{\text{chel}(g)} = -2E(\text{O-H}) + 4E(\text{Ni-N}) + E(\text{H-H}) + 2E(\text{O-H}\cdots\text{O})$ 

Fig. 1.—Thermochemical cycle for the empirical evaluation of coördinate bond energies in bis-(dimethylglyoximato)-nickel(II).

pound but was always within  $\pm 0.5\%$ , with an average of  $\pm 0.33\%$ . The Washburn corrections were omitted since they were smaller than the experimental uncertainty. The combustion products were taken as CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, and either Ni or NiO. The solid residues from the combustion experiments were analyzed for their total nickel content by the standard gravimetric procedure.<sup>2</sup> The analyses are presented in Table I.

It was necessary to obtain the heats of combustion of three of the ligands in order to calculate their heats of formation. The picolinic acid and 8-hydroxyquinoline used were reagent grade materials. The dimethylglyoxime was prepared by the acidification of a solution of the reagent-grade sodium salt. Calcd. for  $C_4H_8O_2N_2$ : C, 41.37; H, 6.94. Found: C, 41.40; H, 6.76.

The vapor pressures of the nickel chelates and the parent ligands were determined over a range of temperatures by the isoteniscope method as modified by Burg and Truemper.<sup>3</sup> Each compound was made into a pellet using a pressure of 5000 p.s.i. From these pellets, small portions were taken and introduced into the isoteniscope. Due to the nature of these compounds, the reproducibility of the vapor pressure measurements was rather poor. As a result the heats of vaporization obtained are the best estimates that could be made. A calibration run with benzoic acid gave vapor pressures of 1.1 mm. at 94.8°, 1.9 mm. at 107.0°, and 2.7 mm. at 112.3°. The literature vaules for these temperatures are 0.94, 1.85, and 2.44 mm., respectively.<sup>4</sup>

#### **Results and Discussion**

The measured heats of combustion for both the nickel complexes and the ligands are presented in Table II. The heats of sublimation are presented in Table III.

The bond energies were calculated using thermochemical cycles of the sort described earlier.<sup>1</sup> The cycle used for the nickel(II) complex with dimethylglyoxime is given in Fig. 1. The results of these calculations are summarized in Table IV.

## TABLE III

#### HEATS OF SUBLIMATION (KCAL./MOLE)

	$\Delta H_{3}$		$\Delta H_2$
Compound	vap.	Compound	vap.
Bis-(acetylacetonato)-nickel(II)	$16.5^a$	Acetylacetone	$11.5^{a}$
Bis-(dimethylglyoximato)-nickel(II)	7.7	Dimethylglyoxime	6.9
Bis-(glyoximato)-nickel(II)	13.4	Glyoxime	41.0
Bis-(salicylaldehydato)-nickel(II)	20.4	Salicylaldehyde	$11.4^{b}$
Bis-(salicyliminato)-nickel(II)	37.8	Salicylimine	$12.0^{c}$
Bis-(8-quinolinato)-diaquonickel(II)	16.8	8-Quinolinol	$40.3^{d}$
Bis-(picolinato)-nickel(II)	18.3	Picolinic acid	21.0
Bis-(glycinato)-nickel(II)	8.1	Glycine	9.9

<sup>a</sup> J. W. Truemper, Thesis, Louisiana State University, Baton Rouge, 1959, mic. 59-5529, University Microfilm, Ann Arbor, Mich. <sup>b</sup> D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947). <sup>c</sup> Estimated on basis of value for salicylaldehyde. <sup>d</sup> Calculated from an estimated value of 30 kcal. for the heat of fusion. This value is close to that for similar compounds ("Handbook of Chemistry and Physics," Cleveland, Ohio, 41st Ed., 1959, pp. 2315–2317). The heat of vaporization of the liquid was found to be 10.44 kcal./mole.

The bond energies for the Ni–O bonds fall in the range 56.8 to 71.8 kcal, that of the Ni–N bond is close to 57 kcal. The average value for the Ni–O bond in the acetylacetonate complex was calculated on the basis of the structure given by Bullen, *et al.*<sup>5</sup> Solid "nickel-(II)acetylacetonate" is a trimeric structure with each nickel octahedrally surrounded by six oxygen atoms. The value for the salicylaldehyde complex was calculated for two structures. The first of these is based upon a square planar structure for the complex in the vapor phase. The second is calculated on the assumption that the nickel is octahedrally coördinated in the vapor phase as is known to be the case in the solid.<sup>6</sup> The first assumption seems preferable.

(5) G. J. Bullen, R. Mason, and P. Pauling, Nature, 189, 291 (1961).

<sup>(3) (</sup>a) E. W. Burg and J. W. Truemper, J. Phys. Chem., 64, 487 (1960);
(b) J. W. Truemper, Ph.D. Thesis, Louisiana State University, Baton Rouge, 1959, MiC59-5529, University Microfilms, Ann Arbor, Michigan.
(4) "International Critical Tables," Vol. III, McGraw-Hill Book Co.,

<sup>(4) &</sup>quot;International Critical Tables," Vol. 111, McGraw-Hill Book Co., New York, N. Y., 1928, p. 208.

<sup>(6)</sup> F. K. C. Lyle, B. Morosin, and E. C. Lingafelter, Acta Cryst., 12, 938 (1959).

TABLE IV						
Compound	$\Delta H_{f,L}$	$\Delta H_{\rm chel}$ (g)	$\Delta H_{\mathbf{f}}$ , complex	$\Delta H_{\mathbf{ox}}$	Bond energy	σ <sup>i</sup>
Bis-(acetylacetonato)-nickel(II)	$-100.95^{a}$	-314.0	-413.18	-1476.3	(Ni-O) = 71.8	0.7
Bis-(dimethylglyoximato)-nickel(II)	-38.92	-159.6	-140.03	-1288.4	$(Ni-N) = 56.2^{f}$	1.5
Bis-(glyoximato)-nickel(II)	$-21.1^{b}$	-165.65	-108.44	- 600.8	$(Ni-N) = 57.8^{f}$	2.9
Bis-(salicylaldehydato)-nickel(II)	- 66.73°	-157.7	-197.8	-1715.6	$(Ni-O) = 68.7(45.8)^{h}$	1.3
Bis-(salicylaldiminato)-nickel(II)	$-50.0^{d}$	-120.5	-190.3	-1733.8	$(Ni-O) = 60.3^{g}$	2.2
Bis-(8-quinolinato)-diaquonickel(II)	-51.73	-125.7	- 84.09	-2218.3	$(Ni-O) = 64.4^{g}$	1.7
Bis-(picolinato)-nickel(II)	-82.45	-112.4	-221.0	-1400.9	$(Ni-O) = 57.8^{g}$	4.5
Bis-(glycinato)-nickel(II)	$-124.73^{e}$	-110.4	-290.57	- 649.1	$(Ni-O) = 56.8^{a}$	3.5

<sup>a</sup> G. R. Nicholson, J. Chem. Soc., 2431 (1957). <sup>b</sup> N.B.S. Circular 500, Table 23-47, p. 144. <sup>c</sup> Calculated from the value of the heat of combustion: "Handbook of Chem. and Phys.," 29th Ed., p. 1462. <sup>d</sup> Estimated on the basis of the value for salicylaldehyde. <sup>e</sup> "International Critical Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1928, p. 167. <sup>f</sup> Calculated using 26 kcal. for (O-H···O) bond in the compound. <sup>g</sup> Calculated using average value of (Ni-N) bond. <sup>h</sup> Calculated value based on an octahedral complex. <sup>i</sup> Calculated using average value of (Ni-N) bond. <sup>h</sup> Calculated value based on an octahedral complex. <sup>i</sup> Calculated using average value of (Ni-N) bond. <sup>h</sup> Calculated value based on an octahedral complex. <sup>i</sup> Calculated value babsed on an octahedral complex. <sup>i</sup> Calculated value based on an o culated as described in the text.

The complexes with glyoxime and dimethylglyoxime present a special problem because of the occurrence of very strong hydrogen bonds in both the solid and gaseous complexes. Since the hydrogen bond is formed when the complex is formed, its energy enters into the term designated  $\Delta H_{chel(g)}$  in Fig. 1. An estimate of the bond strength of this hydrogen bond was made on the basis of the bond distance and bond strengths in other hydrogen bonds. Using values for several -O-H. . . O bonds as well as one F-H. . . N bond given by Ketelaar,<sup>7</sup> a graph of the bond energy vs. log of O-H...O bond length was prepared. Using the O-H. . . O distance for the dimethylglyoxime complex given by Godycki and Rundle<sup>8</sup> a bond energy of 26 kcal. was estimated for this hydrogen bond from the graph. An average of the two Ni–N bond energies was then used to calculate the Ni-O bond energies in the remainder of these compounds where the two types of bonds were present simultaneously. In the case of salicylaldimine, the heats of formation and sublimation of the ligand where estimated. This ligand is extremely unstable unless coördinated and does not lend itself to the direct calorimetric studies.

The values reported for the heats of sublimation are not as accurate as those given for the heats of combustion. This arises primarily from the concurrent thermal decomposition which occurred in some cases, as well as the experimental (manipulative) difficulties. These values are useable in this application since the error they introduce constitutes only a small fraction of the final bond energy.

In the calculation of the bond energies, the O-H bond energy was taken as 110 kcal./mole and the H-H bond energy as 103 kcal./mole. The heat of vaporization of solid nickel was taken as 91 kcal./mole,<sup>9</sup> and the energy

of transition from the keto to the enol form of acetylacetone was taken as 2.61 kcal./mole.<sup>10</sup> The heats of formation of these chelates and some of the ligands were also calculated and these values are also presented in Table IV.

The values of the bond energies collected in Table IV show an encouraging consistency. The variation in the bond energies for the different complexes shows that structural features have a definite effect, but certainly not a greater effect than is found in organic compounds.

The values for the standard deviations given for the bond energy terms in Table IV were calculated from the standard deviations of the terms used in the thermochemical cycle by a standard method.<sup>11</sup> As an illustration, the values for the standard deviations of the terms found in Fig. 1 are

 $\Delta H_{1,\text{vap.}}$ , taken as a known quantity,  $\sigma = 0$ (1)

$$\Delta H_{2,\text{vap.}}, \ \sigma = 1.3 \tag{2}$$

$$\Delta H^{0}_{f,L}, \ \sigma = 1.5 \tag{3}$$

$$\Delta H_{\rm ox}, \, \sigma = 0 \tag{4}$$

$$\Delta H_{3}, \sigma = 0.4 \tag{5}$$

$$\Delta H_{\rm e}, \, \sigma = 3.5 \tag{6}$$

$$\Delta H_{\rm chel(g)}, \ \sigma = 5.3 \tag{7}$$

$$E(O-H...O), \sigma = 5.0 \text{ (estimated)}$$
(8)

The values of E(O-H) and E(H-H) are taken as known quantities,  $\sigma = 0$  (all in kcal./mole).

Acknowledgment.--This work was supported by a grant from the U.S. Atomic Energy Commission, for which we wish to express our thanks.

(10) B. Jakuszewski and M. Lazniewski, Bull. Acad. Polon. Sci., Ser. Sci., Chim., Geol., et Geograph., 7, 177 (1959); Chem. Abstr., 54, 16161 (1960).
(11) F. D. Rossini, Ed., "Experimental Thermochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chapt. 14, p. 309.

<sup>(7)</sup> J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., Amsterdam, 1958, p. 416.
(8) L. E. Godycki and R. E. Rundle, Acta Cryst., 6, 487 (1953).

<sup>(9)</sup> National Bureau of Standards Circular 500, Table 45-1, p. 245.