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DEPARTMENT OF CHEMISTRY
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The Preparation of Complex Compounds of Certain Organic Bases with Nickel(II) and Cobalt(II) Oxalate and Phthalate and the Determination of Their Heats of Formation[1]

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The effect of the negative ions in nickel(II) and cobalt(II) salts upon the heat of formation of pyridine complexes of these salts and the effect of the character of the complexing amine upon the heat of formation of complexes with nickel(II) thiocyanate have been reported.[3] A new series of nickel and cobalt compounds have been prepared to determine the effect of aromatic and aliphatic dibasic negative groups upon the heat of formation of the complexes. The heats of formation of the complexes were calculated according to the equation

$$\Delta H_f = L_S + L_A - L_C$$

from the observed values of the heats of reaction of the simple salt, the amine and the complex with 2 *N* HCl.

Preparation of the Compounds

Nickel(II) and Cobalt(II) Oxalates.—These salts were prepared by conventional methods and analyzed for metal content. *Anal.* Calcd. for NiC_2O_4: Ni, 40.04. Found: Ni, 39.85. Calcd. for CoC_2O_4: Co, 40.10. Found: Co, 40.32.

Nickel(II) and Cobalt(II) Phthalates.—The phthalates were prepared by refluxing for six hours a mixture of nickel or cobalt carbonate with an equivalent amount of phthalic acid solution. Any residue remaining after six hours was removed by filtration and the filtrate evaporated to dryness. Nickel phthalate formed as yellow green crystals; the cobalt phthalate as lavender crystals. *Anal.* Calcd. for $NiC_8H_4O_4$: Ni, 26.34. Found: Ni, 26.25. Calcd. for $CoC_8H_4O_4$: Co, 26.42. Found: Co, 26.68.

Oxalatodipyridinenickel(II) and Oxalatodipyridinecobalt(II); Oxalatobis(β- or γ-picoline)-nickel(II) and Oxalatobis(β- or γ-picoline)-cobalt(II).—The complex salts were formed by adding excess of each of the amines to the metal oxalates. The light blue crystals of nickel complexes and the rose-colored crystals of cobalt complexes formed by the evaporation of excess amine were stored in desiccators until equilibrium was reached. *Anal.* Calcd. for $NiC_2O_4 \cdot 2C_5H_5N$: Ni, 19.25. Found: Ni, 19.36. Calcd. for $NiC_2O_4 \cdot 2\beta C_6H_7N$: Ni, 17.63. Found: Ni, 17.70. Calcd. for $NiC_2O_4 \cdot 2\gamma C_6H_7N$: Ni, 17.63. Found: Ni, 17.50. Calcd. for $CoC_2O_4 \cdot 2C_5H_5N$: Co, 19.31. Found: Co, 19.22. Calcd. for $CoC_2O_4 \cdot 2\beta C_6H_7N$: Co, 17.69. Found: Co, 17.79. Calcd. for $CoC_2O_4 \cdot 2\gamma C_6H_7N$: Co, 17.69. Found: Co, 17.54.

Phthalatotetrapyridinenickel(II) and Phthalatotetrapyridinecobalt(II).—The phthalate pyridine–metal complexes were prepared in a manner identical to that described for the complex oxalates. These complexes were soluble in chloroform and could be recrystallized from that solvent with no change in composition. The complex containing nickel formed as bright blue crystals; the cobalt complex was rose-colored.

Phthalatotetrakis-(β- or γ-picoline)-nickel(II) and Phthalatotetrakis(β- or γ-picoline)-cobalt (II).—These were prepared by adding a slight excess of each of the amines to water solutions of the metal phthalates. The resulting complex compounds were extracted with chloroform. The crystals resulting from the evaporation of the solvent were freed from excess amines and stored in desiccators. The color of the phthalato-β-picolinenickel complex was light blue; the analogous compound containing γ-picoline formed blue-green crystals. The color of both of the cobalt complex compounds was deep red. *Anal.* Calcd. for $NiC_8H_4O_4 \cdot 4C_5H_5N$: Ni, 10.88. Found: Ni, 10.66. Calcd. for $NiC_8H_4O_4 \cdot 4\beta C_6H_7N$: Ni, 9.86. Found: Ni, 9.67. Calcd. for $NiC_8H_4O_4 \cdot 4\gamma C_6H_7N$: Ni, 9.86. Found: Ni, 9.80. Calcd. for $CoC_8H_4O_4 \cdot 4C_5H_5N$: Co, 10.92. Found: Co, 10.88. Calcd. for $CoC_8H_4O_4 \cdot 4\beta C_6H_7N$: Co, 9.90. Found: Co, 9.98. Calcd. for $CoC_8H_4O_4 \cdot 4\gamma C_6H_7N$: Co, 9.90. Found: Co, 10.07.

Determination of Heats of Reaction.—A method similar to that reported earlier[3] was used to determine the heats of reaction of the simple salts, the amines and the complexes with 2 *N* HCl. The values of the heats of reaction obtained and the calculated heats of formation are recorded in Table I.

TABLE I

Substance	Heat of soln., cal./mole at 25° [a]	Heat of formation, cal./mole at 25° [a]
Pyridine [b]	− 8,530 (± 10)	
β-Picoline	− 9,210 (± 30)	
γ-Picoline	− 9,400 (± 20)	
NiC_2O_4	− 3,460 (± 20)	
$NiC_8H_4O_4$	−10,940 (± 30)	
CoC_2O_4	− 5,070 (± 30)	
$CoC_8H_4O_4$	− 7,010 (± 20)	
$NiC_2O_4 \cdot 2Py$	− 1,340 (± 10)	19,200
$NiC_2O_4 \cdot 2\beta Pic$	− 2,020 (± 20)	19,900
$NiC_2O_4 \cdot 2\gamma Pic$	− 2,210 (± 20)	20,000
$NiC_8H_4O_4 \cdot 4Py$	−10,260 (± 40)	34,800
$NiC_8H_4O_4 \cdot 4\beta Pic$	−12,500 (±100)	35,300
$NiC_8H_4O_4 \cdot 4\gamma Pic$	−19,440 (± 20)	29,100
$CoC_2O_4 \cdot 2Py$	− 1,280 (± 40)	20,800
$CoC_2O_4 \cdot 2\beta Pic$	− 4,500 (± 90)	19,000
$CoC_2O_4 \cdot 2\gamma Pic$	− 5,080 (± 10)	18,800
$CoC_8H_4O_4 \cdot 4Py$	−12,340 (± 30)	28,800
$CoC_8H_4O_4 \cdot 4\beta Pic$	−12,710 (± 30)	31,100
$CoC_8H_4O_4 \cdot 4\gamma Pic$	−13,080 (±100)	31,500

[a] Averages obtained from 2 to 4 determinations on each compound. [b] Corrected value (ref. 3*b*).

The heats of formation of the oxalate complexes formed with each of the three amines and nickel(II) or cobalt(II), Table I, show *no great variance* between the metals used nor with the amines added to form the complexes. These results are in agreement with the work previously reported.[3a,b]

The heats of formation of the phthalate complexes show less uniformity in the values observed. The heat of solution of phthalatotetrakis(γ-picoline)-nickel(II) appears to be anomalously high resulting in a low calculated heat of formation of the complex. Since the phthalato complex contained four molecules of the bases, a direct comparison with the oxalates cannot be made to determine the effect of the negative group. However, in comparing the heats of formation of the three phthalatotetraaminenickel(II) complexes with the corresponding thiocyanatotetraaminenickel(II) complexes reported earlier,[3b] it is observed that the heats of formation of the thiocyanato complexes are higher.

It has been noted[3b] that when attempts were made to crystallize the thiocyanate complexes of β- and γ-picolinenickel(II) from chloroform solution some entrapment of chloroform within the crystals was observed. In the preparation of the oxalate and phthalato complexes, it was thought that perhaps the dibasic organic negative groups might increase the entrapment of the solvent. No similar

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[2] This article is based on a thesis submitted by Albert B. Costa in partial fulfillment of the requirements for the degree of Master of Science, Oregon State College.

[3] (a) A. V. Logan, D. C. Bush and C. J. Rogers, THIS JOURNAL, **74**, 4194 (1952); (b) A. V. L. and D. W. Carle, *ibid.*, **74**, 5224 (1952).

entrapment of the solvent was observed. The thiocyanato-(β- and γ-)-picolinenickel(II) complex compounds have been the only ones of many tested in this Laboratory which have so markedly exhibited this property.

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Methyl Affinities of Non-planar Aromatic Hydrocarbons

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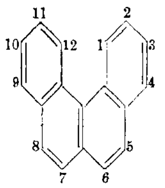
It was shown in a previous communication[1] that methyl radicals add to aromatic compounds, such an addition being initiated by reaction (1)

$$A + CH_3 \longrightarrow A{\cdot}CH_3 \qquad (1)$$

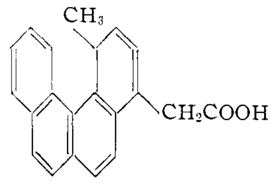
The relative rate constants of reaction (1), referred to as methyl affinities, were measured for a series of aromatic hydrocarbons, and it was found that their magnitudes are greatly affected by the structure of the aromatic compound. Thus, the following values were reported[1] for the methyl affinities of benzene, naphthalene, anthracene and naphthacene, namely: 1, 22, 820 and 9250, respectively.

Methyl affinities may be correlated to various properties of aromatic molecules; for example, it was shown by Szwarc[2] that logarithms of methyl affinities vary linearly with the singlet–triplet excitation energies; a similar relation was established by Coulson[3] for localization energies, while Matsen[4] correlated methyl affinities to electron affinities and ionization potentials. The correlation between the constitution of an aromatic molecule and its methyl affinity could be better understood by investigating systematically the effects of various structural changes on methyl affinity. In this communication, we shall deal with effects caused by the deviation of a molecule of an aromatic hydrocarbon from its planar configuration.

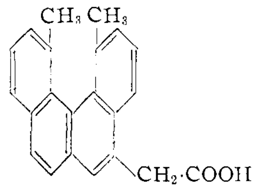
Certain aromatic hydrocarbons as, *e.g.*, some substituted benzo(c)phenanthrenes, can be caused to become non-planar as a result of intramolecular overcrowding.[5] The unsubstituted benzo(c)phenanthrene (I) has been shown to be non-planar in the solid state.[6] The non-planarity of substituted benzo(c)phenanthrenes is proved by partial resolution and facile racemization of 1-methylbenzo(c)phenanthrene-4-acetic acid[5] (II) and further evidence has been provided recently by resolution of 1,12-dimethylbenzo(c)phenanthrene-5-acetic acid (III) which has been shown to be optically stable, even at higher temperatures.[7] The increasing optical stability of these compounds provides evidence of increasing internal strain and hence increasing non-planarity of the molecules.



I



II



III

The methyl affinities of all of the methyl benzo(c)phenanthrenes, as well as of I and of 1,12-dimethylbenzo(c)phenanthrene, have been determined and are listed in Table I. The methyl affinities of the 2-, 3-, 4-, 5- and 6-methylbenzo(c)phenanthrenes are roughly the same and about equal to that of the parent hydrocarbon I. However, the methyl affinity rises somewhat in 1-methylbenzo(c)phenanthrene and considerably in 1,12-dimethylbenzo(c)phenanthrene. Since this order is that of increasing strain due to intramolecular overcrowding,[8] it appears that an increase in departure from a coplanar structure for aromatics leads to an increase in methyl affinity. Probably the deformation increases the localization of the electrons which are usually delocalized in aromatic rings and hence leads to increased availability of electrons for reaction with free radicals.

TABLE I

METHYL AFFINITIES OF BENZO(c)PHENANTHRENE AND ITS DERIVATIVES

Solvent, toluene; $T = 85°$.

Benzo(c)phenanthrene[a]	Mole %	CH_4/CO_2	k_{II}/k_I	Methyl affinity
Non-substituted	2.1	0.562	8.5	64
2-Methyl-	4.3	.506	7.2	55
3-Methyl-	4.3	.475	9.1	68
3-Methyl-	4.0	.475	9.8	73.5
4-Methyl-	4.3	.467	9.7	73
5-Methyl-	4.3	.496	7.8	58.5
6-Methyl-	4.3	.508	7.1	53.5
6-Methyl-	4.0	.474	9.9	74
1-Methyl-	4.3	.405	14.4	108
1-Methyl-	3.1	.459	14.2	107
1,12-Dimethyl-	4.0	.330	24.5	184
1,12-Dimethyl-	4.0	.330	24.5	184
1,12-Dimethyl-	4.0	.333	24.2	181

[a] The numeration of positions in benzo(c)phenanthrene is shown in I.

JOINT CONTRIBUTION FROM
DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF NEW YORK
COLLEGE OF FORESTRY
SYRACUSE, NEW YORK, AND
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COLUMBUS, OHIO

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