Conclusions

We have shown that constant values of K_σ and K_π can be employed to scale predicted values of $\Psi^2(0)$ from extended Hückel calculations to experimental values of the epr coupling constants. The results lend quantitative support to the qualitative predictions of geometry made directly from epr spectral interpretations.[15] The agreement between calculated and experimental values of a_H is excellent considering the approximations made. We have assumed that when $\theta = 20°$ or more there is no contribution to the measured coupling constant from an indirect type interaction. We have also assumed that all coupling constants treated by the direct interaction are positive. This is a good assumption for large values of a_H, but the small values of a_H could be negative with significant contributions from exchange-type interactions. Consequently, we are satisfied with the degree of correlation obtained and question the wisdom of trying further to improve the agreement by variation of the parameters in the MO calculation at this level of sophistication, *i.e.*, without taking explicit account of higher state mixing.

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Reactions of Coordinated Ligands. XIV. Reactions of Tris(diamine)nickel(II) Ions with Various Carbonyl Compounds, Especially β-Hydroxy Ketones and Aldehydes

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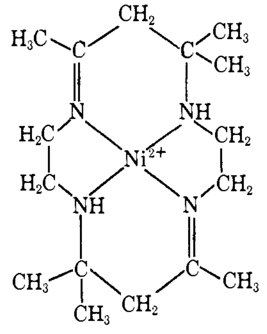
Abstract: Under various conditions, mesityl oxide, diacetone alcohol, and acetone all react with tris(ethylenediamine)nickel(II) salts to yield either the macrocyclic complex 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-dienenickel(II) or the complex of a long-chain tetradentate, 1,9-diamino-4,6,6-trimethyl-3,7-diazanona-3-enenickel(II). The reaction also occurs for a β-hydroxyaldehyde and various β-hydroxy ketones containing primary, secondary, and tertiary alcohol groups. The same product (1,9-diamino-6-methyl-3,7-diazanona-3-enenickel(II) tetrachlorozincate) is obtained by reaction of tris(ethylenediamine)nickel(II) salts with acetaldehyde, aldol, and crotonaldehyde. The corresponding compounds from tris(1-propylenediamine)nickel(II) tetrachlorozincate are also described. This general reaction provides a very useful route to the synthesis of chelate rings containing desired arrangements of substituents. The β-hydroxy ketone route is probably preferable to the reactions based on the condensations of simple carbonyl compounds.

The use of the reactions of coordinated ligands for the synthesis of useful and unusual ligands has seldom been exploited. One of the more fully developed examples of this controlled approach to ligand synthesis is contained in the work of Curtis and his co-workers. These researchers have shown that tris(ethylenediamine)nickel(II) perchlorate will dissolve in acetone and then react with the solvent to form the macrocyclic complex I (isolated as the perchlorate).[1]



I

Most recently it has been shown that the free ligand may be prepared either from the analogous iron(II) system[2] or by reaction of en·$HClO_4$ with mesityl oxide under mild conditions.[3] The latter represents an application of a reaction first reported from this laboratory.[4] The isomers of the nickel(II) complex have been fully characterized.[5–7]

Reduction of I and separation of the reduced ligand yields a second interesting macrocycle II.[8] House and Curtis[9] have also demonstrated that, under different conditions, tris(ethylenediamine)nickel(II) ion reacts with acetone to give the cation III. Since these and related reactions may hold for the preparation of aliphatic tetramines in general and because of the unusual nature of the products, we[4] have studied new synthetic routes to I and III using diacetone alcohol

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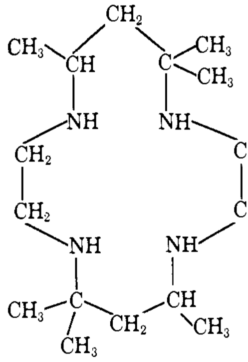
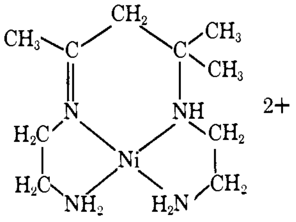


II



III

(4-hydroxy-4-methyl-2-pentanone) and mesityl oxide, as well as acetone. The synthesis has been extended to the compound derived from tris(1-propylenediamine)-nickel(II) chloride.

In order to show the generality of the condensation reactions reported here, homologs of I were prepared using various simple ketones and aldehydes and also various hydroxy ketones and corresponding α,β-unsaturated ketones. Curtis and co-workers have shown that methyl ethyl ketone reacts with tris(ethylenediamine)nickel(II) chloride dihydrate to give an analog of I on heating the reactants together at 100° for several hours.[10] They also report that reactions using propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde all lead to analogs of I with various alkyl substituents.[9]

In this work we show the broad generality of the reaction of tris(ethylenediamine)nickel(II) salts with β-hydroxy ketones to form compounds like III. The reaction proceeds smoothly with β-hydroxy ketones containing primary, secondary, and tertiary alcohol groups. Also the β-hydroxyaldehyde, aldol, reacts to give the same product as that obtained from acetaldehyde or crotonaldehyde.

We have not succeeded in extending the reaction to diamine compounds or hydroxy ketones with longer bridges between the functional groups. Reactions with α-hydroxy ketones do proceed, but substantially different products are obtained and these are described in a separate publication.

New Routes to the Synthesis of Known Compounds. Reaction of tris(ethylenediamine)nickel(II) chloride dihydrate with diacetone alcohol by refluxing the heterogeneous mixture of the two in the absence of solvent yields, as the apparent exclusive product, the macrocyclic complex I as the chloride dihydrate. The identity of this material was confirmed by elemental analyses and the exact congruence of its infrared spectrum with the spectrum of the chloride dihydrate obtained from the perchlorate of I by metathesis.[9]

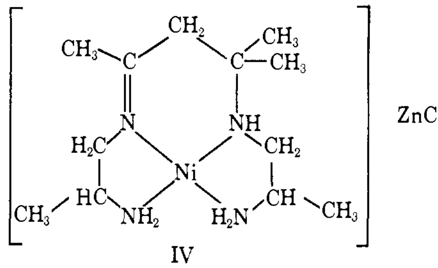
When the corresponding reaction is carried out using excess mesityl oxide the results are different. There is considerable deterioration of the mesityl oxide and the only nickel-containing product which can be isolated is III, as the chloride. This product was converted by metathesis to the tetrachlorozincate salt and identified by comparison with the same compound derived from acetone.[9]

The preparation of III from acetone has been greatly improved by treating tris(ethylenediamine)nickel(II) chloride dihydrate with acetone in methanol solution. After several hours, the reaction is essentially complete and the product is most easily isolated by adding zinc chloride and allowing the tetrachlorozincate salt to crystallize. However, if the product is fractionally precipitated by the addition of ether, a good yield of III is obtained as the chloride monohydrate, along with a small amount of I, as the chloride dihydrate. If the reaction is interrupted at an earlier stage, some starting material can be recovered.

The reactions of both diacetone alcohol and mesityl oxide with tris(ethylenediamine)nickel(II) chloride dihydrate and zinc chloride in refluxing methanol–ethylene glycol result in good yields of III as the tetrachlorozincate salt. The reaction with mesityl oxide has been studied in some detail, and it is noteworthy that, if zinc chloride is excluded, the reaction proceeds, in the course of several days, to give a mixture of I and III which can be separated by fractionation using ether. If tris(ethylenediamine)nickel(II) iodide is allowed to react with mesityl oxide by refluxing in methanol for several days, the iodide of the macrocyclic complex may be separated in a crystalline highly pure form.

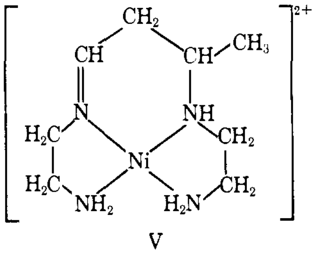
Both I and III appear to be present during most stages of these reactions, but in varying ratios. The material isolated most readily from any given reaction depends on the nature of the anion. Perchlorate and iodide lead to isolation of the macrocyclic complex I, while tetrachlorozincate and chloride favor the early precipitation of III.

The reactions of tris(1-propylenediamine)nickel(II) chloride dihydrate with acetone or diacetone alcohol in methanol yield only one product, and this is postulated to have the structure IV. The positions of the methyl groups are dictated by steric considerations and by the fact that pmr spectrum shows only one methyl doublet while alternate arrangements would put these methyls into very different environments which should give rise to two doublets.



IV

Synthesis of New Compounds. When acetone is replaced with acetaldehyde in the reaction with tris(ethylenediamine)nickel(II) salts, a reaction is observed to occur but a product can be isolated only if the amount of acetaldehyde is limited to 2 molar equiv. With this condition a good yield of V can be obtained. The same compound appears to be the only product from the reaction of the $[Ni(en)_3]^{2+}$ ion and aldol VI or crotonaldehyde. Apart from the elemental analyses,



V

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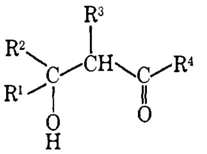
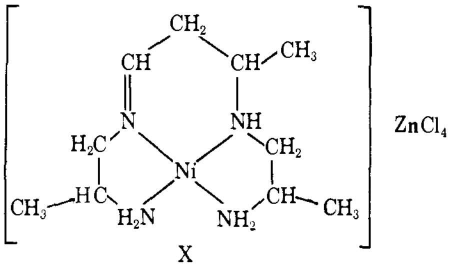
(10) M. M. Blight, Ph.D. Thesis, University of New Zealand, 1957.



	R^1	R^2	R^3	R^4
VI	H	CH_3	H	H
VII	H	CH_3	H	CH_3
VIII	H	H	H	CH_3
IX	H	H	CH_3	CH_3

the most convincing proof of the identity of the products from these three different reagents is the complete superimposability of their infrared absorption curves. When excess acetaldehyde is used, intractable oils invariably result, possibly because of a side reaction involving the polymerization of the excess aldehyde, or possibly because of the formation of macrocyclic complexes like those obtained in the reaction with acetone.[1] We were unable to isolate such compounds.

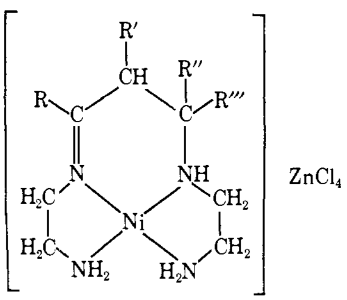
In contrast, little trouble is experienced in isolating the product X from the reaction between acetaldehyde and tris(1-propylenediamine)nickel(II) tetrachlorozincate, even when excess aldehyde is used. The product in this case is tentatively formulated in the isomeric modification given in X. This structure explains why this system is not complicated by rapid onset of further reaction. The terminal amines are attached to secondary carbon atoms and are expected to react much more slowly than the primary substituted amine groups present in V. As implied, subsequent reaction of V with excess of the reagent could cause the formation of a mixture of products which is difficult to separate.



X

The reaction of aldol with tris(ethylenediamine)-nickel(II) tetrachlorozincate demonstrates that, just as simple aldehydes can replace acetone[9] in reactions which yield homologs of I, so a β-hydroxyaldehyde can replace the β-hydroxy ketone in the related reaction described above. Furthermore aldol contains a secondary alcohol group evidencing further generality of the reaction with respect to substitution at the carbinol carbon atom.

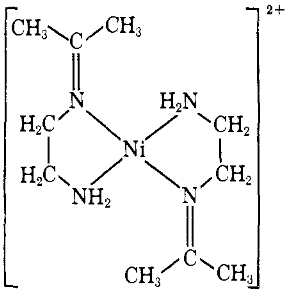
A series of β-hydroxy ketones, VII, VIII, and IX, has been investigated by reaction with tris(ethylenediamine)nickel(II) chloride dihydrate in the presence zinc chloride, following a procedure similar to that described for the preparation of III from diacetone alcohol. These reactions gave XI, XII, and XIII, respectively. While quantitative measurements were not made, it is clear that these reactions all proceed at about the same rate. The initial precipitate of tris-(ethylenediamine)nickel(II) tetrachlorozincate dissolves over a period of about 3 hr in each case. If the replacement of the hydroxy group was a rate-controlling step, one should see pronounced differences in rates, with the tertiary or primary alcohol reacting faster depending on whether the reaction proceeded by an S_N1 or S_N2 mechanism.



XI, $R = CH_3$; $R' = H$; $R'' = CH_3$; $R''' = H$
XII, $R = CH_3$; $R' = H$; $R'' = H$; $R''' = H$
XIII, $R = CH_3$; $R' = CH_3$; $R'' = H$; $R''' = H$
III, $R = CH_3$; $R' = H$; $R'' = CH_3$; $R''' = CH_3$

It is interesting to note that extension of the synthesis involving β-hydroxy ketones to γ-hydroxy ketones was unsuccessful. Tris(ethylenediamine)nickel(II) ion appears to be destroyed in the presence of 1-hydroxy-4-pentanone (the methanol solution changes color under reflux to a pale green which is reminiscent of the simple solvated Ni^{2+} ion).

When tris(ethylenediamine)nickel(II) salts are replaced with tris(trimethylenediamine)nickel(II) salts, no reaction is observed with diacetone alcohol, even after 3 days, and the starting material can be recovered in high yield. It is probably significant that there is a difference between the reaction of acetone with these diamine complexes in that the ethylenediamine complex gives III as its other main derivative, while the trimethylenediamine compound yields compound XIV in which two acetone molecules are attached independently as isopropylidene groups.[11]



XIV

The factors preventing the formation of the three-carbon bridge in this case are probably also responsible for the inertness of tris(trimethylenediamine)nickel(II) ion toward diacetone alcohol. We believe that this selectivity is simply steric in origin and that formation of the new chelate ring between the two trimethylenediamine ligands would lead to the formation of a very crowded fused ring system. The thermodynamic equilibrium established at some early stage of the reaction between tris(trimethylenediamine)nickel(II) ion and diacetone alcohol apparently strongly favors the starting material. In the case of the reaction with acetone an alternative process leads to the energetically preferred product XIV.

The closure of chelate rings utilizing the full series of β-hydroxy ketones and a single β-hydroxyaldehyde makes available a more versatile and more readily controlled reaction than the previously reported condensation with acetone and other simple carbonyl

(11) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **86**, 223 (1964).

compounds. The new reaction is particularly useful in producing chelate rings with substituent groups located at desired positions.

In the case of 4-hydroxy-2-pentanone, no dissociation of the β-hydroxy ketone occurs prior to reaction, for such a process would provide a mixture of acetaldehyde and acetone. We have shown that when mixtures of acetaldehyde and acetone are allowed to react with tris(ethylenediamine)nickel(II) ion, the acetaldehyde dominates the process forming XII, the same product formed by aldol or by acetaldehyde alone. In contrast, 4-hydroxy-2-pentanone forms XI. It is concluded that this very general reaction does indeed involve the β-hydroxy ketone.

The relatively poor synthetic results obtained with the unsaturated ketone mesityl oxide suggest that attention should be focused on β-hydroxycarbonyl compounds in future syntheses. It is not unlikely that such materials form as intermediates in the corresponding reaction with such simple carbonyl compounds as acetaldehyde and acetone.

Experimental Section

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-dienenickel(II) Iodide from Mesityl Oxide. Tris(ethylenediamine)nickel(II) iodide is obtained by mixing a saturated solution of potassium iodide (1 g) in methanol with a solution of tris(ethylenediamine)nickel(II) chloride dihydrate (1 g) in methanol and filtering the product. This material is suspended in methanol (100 ml) which contains mesityl oxide (4 ml) and the mixture is refluxed for 3 days. On cooling the reaction mixture and scratching the sides of the flask with a glass rod the iodide separates (yield 0.26 g). It may be necessary to add a little ether while cooling and scratching to initiate the crystallization. Addition of zinc iodide to the filtrate yields the tetraiodozincate (yield 0.6 g). Recrystallization of the iodide from hot ethanol gives beautiful yellow crystals which are stable in concentrated hydrochloric acid solution and give an infrared spectrum consistent with this structure.

Anal. Calcd for $NiC_{16}H_{32}N_4I_2$: C, 32.37; H, 5.39; N, 9.44; I, 42.83; Ni, 9.95. Found: C, 32.11; H, 5.09; N, 9.47; I, 42.67; Ni, 9.91.

5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetrazacyclotetradeca-1,7-dienenickel(II) Chloride Dihydrate. (a) From Diacetone Alcohol. Tris(ethylenediamine)nickel(II) chloride dihydrate (200 mg) is suspended in diacetone alcohol (5 ml) and the mixture is refluxed for 2 days. During this time some yellow product separates and collects around the neck of the flask. The reaction mixture is cooled and mixed with 10 ml of ethanol. Some undissolved starting material is removed by filtering, leaving a yellow solution. Treatment with ether yields two fractions of the desired product; the total yield is 0.17 g. The combined fractions can be recrystallized from ethanol–ether. The compound is soluble in chloroform but cannot be dehydrated in this solvent. The infrared spectrum is identical in all respects with the spectrum of this compound prepared by metathesis from the previously described perchlorate.

Anal. Calcd for $NiC_{16}H_{32}N_4Cl_2 \cdot 2H_2O$: C, 43.05; H, 8.07; N, 12.56; Cl, 15.92. Found: C, 43.00; H, 8.12; N, 12.48; Cl, 15.99.

(b) From Mesityl Oxide. The compound described above is also obtained by careful fractionation of the product of the reaction between tris(ethylenediamine)nickel(II) chloride dihydrate (1.5 g) and mesityl oxide (6 ml) refluxed in methanol (50 ml) for 3 days. Both the dichloride dihydrate of the macrocycle and the dichloride monohydrate of the linear ligand are obtained in this fractionation.

1,9-Diamino-4,6,6-trimethyl-3,7-diazanona-3-enenickel(II) Tetrachlorozincate. (a) From Acetone. Tris(ethylenediamine)nickel(II) chloride dihydrate (10.0 g, 0.0289 mole) is dissolved in 200 ml of methanol. Acetone (40 ml, 0.55 mole) is added and the mixture refluxed for 4 hr. The color of the solution changes from lavender to red-brown. Zinc chloride (10.0 g, 0.0734 mole), dissolved in a minimum of hot methanol, is filtered and added to the red-brown solution. Orange crystals form immediately. The solution is cooled in an ice bath. The product is filtered and dried under a heat lamp; the yield is 10.6 g (78.3%). The orange crystals are recrystallized from a hot 50% ethanol–water mixture.

Anal. Calcd for $NiC_{10}H_{24}N_4ZnCl_4$: C, 25.76; H, 5.19; N, 12.02; Cl, 30.42. Found: C, 25.95; H, 5.22; N, 11.88; Cl, 30.18.

(b) From Diacetone Alcohol. Tris(ethylenediamine)nickel(II) chloride dihydrate (1 g) is dissolved in a mixture of methanol (50 ml) and ethylene glycol (20 ml) and a solution of zinc chloride (1 g, in 20 ml of hot methanol) is added through a fluted filter. 4-Hydroxy-4-methyl-2-pentanone (diacetone alcohol) (1 ml) is added and the inhomogeneous mixture is refluxed for 48 hr. After this time most of the violet starting material has dissolved and a few orange crystals separate from the bright yellow solution. The hot solution is filtered and allowed to cool, yielding some product. Two further fractions are obtained by treating the filtrate with ether: the total yield is 1.1 g (81%). The compound may be recrystallized from hot methanol from which it separates as orange needles.

Anal. Found for $NiC_{10}H_{24}N_2ZnCl_4$: C, 25.94; H, 5.10; N, 11.78; Cl, 30.27.

(c) From Mesityl Oxide. (i) Tris(ethylenediamine)nickel(II) chloride dihydrate (10 g) is dissolved by warming in methanol (200 ml). Mesityl oxide (40 ml) is added and the mixture is refluxed for 20 min. To the deep red solution so formed, zinc chloride (10 g) in methanol 200 ml is added. A mauve precipitate separates. Ethylene glycol (120 ml) is added and the mixture is refluxed for a further 32 hr. The resulting brown solution is filtered, seeded with a few crystals of the product, and set in the refrigerator to cool. The yield of yellow crystalline material is 3.5 g (25%) and its infrared spectrum confirms its identity as the complex of the linear tetradentate ligand.

(ii) The same product is obtained in poor yield as the chloride by direct reaction between tris(ethylenediamine)nickel(II) chloride dihydrate and mesityl oxide under reflux. It is purified by isolation as the tetrachlorozincate(II) salt and recrystallization from hot methanol and was identified by its infrared spectrum.

1,9-Diamino-4,6,6-trimethyl-3,7-diazanona-3-enenickel(II) Chloride Monohydrate. Tris(ethylenediamine)nickel(II) chloride dihydrate (10 g, 0.0289 mole) and acetone (32 g, 0.55 mole) are heated together in refluxing methanol (200 ml) for 4 hr. The product is precipitated from the resulting solution in a number of fractions by adding aliquots of ether. Early fractions contain some of the starting material and residual fractions are found to contain the chloride dihydrate of the macrocyclic complex. Several of the middle fractions (about 3 g) were combined and purified by extraction into 1-butanol. This removes any tris(ethylenediamine)nickel(II) salts which are quite insoluble. The product is recovered from the butanol by precipitation with ether and the cycle is repeated. Final purification is achieved by dissolving the yellow complex in a minimum of water (~1 ml for 1 g) and adding ten times this amount of methanol followed by a large excess of ether. The solution becomes very cloudy but on standing deposits long yellow needles of very pure product.

Anal. Calcd for $NiC_{10}H_{24}N_4Cl_2 \cdot H_2O$: C, 34.48; H, 7.47; N, 16.09; Cl, 20.40; Ni, 16.96. Found: C, 34.60; H, 7.52; N, 16.10: Cl, 20.69; Ni, 16.78.

2,10-Diamino-5,7,7-trimethyl-4,8-diazaundeca-4-enenickel(II) Tetrachlorozincate. Tris(1-propylenediamine)nickel(II) chloride dihydrate (10.0 g, 0.0258 mole) is added to 150 ml of methanol; 41 ml (0.56 mole) of acetone is also added. The resulting solution is refluxed for 66 hr, the color of the solution changing from lavender to red-brown. A filtered solution of 10.0 g (0.0734 mole) of zinc chloride, in a minimum amount of methanol, is added and the mixture is cooled in an ice bath and left in the cold (5°) overnight. The yellow crystals which deposit are removed by filtration and dried under the lamp; yield 10.0 g (80%). Recrystallization from hot 50% ethanol–water gives yellow needles.

Anal. Calcd for $NiC_{12}H_{28}N_4ZnCl_4$: C, 29,16; H, 5.71; N, 11.34; Cl, 28.69. Found: C, 29.05; H, 5.54; N, 11.53; Cl, 28.74.

1,9-Diamino-6-methyl-3,7-diazanona-3-enenickel(II) Tetrachlorozincate. (a) By Reaction with Acetaldehyde. Tris(ethylenediamine)nickel(II) chloride dihydrate (5.0 g, 0.0161 mole) and zinc chloride (5 g) are partially dissolved, by heating, in a mixture of ethanol (250 ml) and ethylene glycol (100 ml). Acetaldehyde (2.5 ml, 2.0 g, 0.046 mole) is added and the mixture is refluxed until all the purple solid (probably $[Ni(en)_3][ZnCl_4]$) is dissolved, usually about 3 hr. The solution is then filtered and allowed to cool. An oil first begins to form on the sides of the flask, but this crystallizes on being rubbed with a glass rod. The product which then separates is quite crystalline. It may be recrystallized from hot methanol; yield 5.2 g (71%).

Anal. Calcd for $NiC_8H_{20}N_4ZnCl_4$: C, 22.02; H, 4.59; N, 12.84; Cl, 32.57. Found: C, 22.26; H, 4.84; N, 12.86; Cl, 32.28.

(b) **By Reaction with Aldol.** Tris(ethylenediamine)nickel(II) chloride dihydrate (2.5 g) is dissolved in 10 ml of ethylene glycol by warming on a water bath. Zinc chloride (2.5 g) is dissolved in ethylene glycol (10 ml) and added to the first solution. One gram of redistilled aldol is added and the volume made up to 50 ml with ethylene glycol. The solution so formed is heated on the water bath for 15 min. The color changes from violet through deep green to reddish orange. The solution is filtered and diluted with 200 ml of ethanol. The oily product which separates solidifies on standing in contact with ethanol overnight. The mother liquor on being cooled overnight yields a yellow-orange crystalline product; the crude yield is 2.45 g (68%). One sample was recrystallized several times from hot methanol.

Anal. Found: C, 21.81; H, 4.63; N, 12.59; Cl, 32.47.

(c) **By Reaction with Crotonaldehyde.** Crotonaldehyde is added (2.2 g, 91% solution) to a mixture of tris(ethylenediamine)nickel(II) chloride dihydrate (5.0 g), zinc chloride (5.0 g), ethanol (250 ml), and ethylene glycol (100 ml). The mixture is heated under reflux for 30 min, filtered, and allowed to cool. A yellow crystalline product separates and is collected at the pump, washed with ethanol and ether, and air-dried. A second crop of crystals is obtained by treatment of the filtrate with ether; the total yield is 3.5 g (57%). The infrared spectra of this compound prepared by these methods are indistinguishable in all details and confirm their identity.

1,9-Diamino-4,6-dimethyl-3,7-diazanona-3-enenickel(II) Tetrachlorozincate. Tris(ethylenediamine)nickel(II) chloride dihydrate (2.5 g) is dissolved in a warm mixture of ethanol (150 ml) and ethylene glycol (100 ml). Zinc chloride (2.5 g) in hot ethanol (50 ml) is added together with 2.5 g of 4-hydroxy-2-pentanone. The mixture is refluxed until all the mauve precipitate has dissolved (about 2 hr) giving a yellow-orange solution. The solution is filtered and allowed to cool overnight at 5°. The crystalline material which separates is collected at the pump and washed with ethanol and ether and dried under the infrared lamp. By the addition of ether to incipient cloudiness, scratching the sides of the flask, and cooling, it is possible to obtain two additional crops of crystalline material; the total crude yield is 3.4 g (*ca.* 100%). A sample was recrystallized from hot methanol.

Anal. Calcd for $NiC_9H_{22}N_4ZnCl_4$: C, 24.00; H, 4.99; N, 12.47; Cl, 31.56. Found: C, 23.81; H, 4.96; N, 12.62; Cl, 31.29.

1,9-Diamino-4-methyl-3,7-diazanona-3-enenickel(II) Tetrachlorozincate. The method described immediately above is followed precisely but with 2.5 g of XII instead of XI. The product is isolated and purified in the same way; the yield is 2.4 g (75%).

Anal. Calcd for $NiC_8H_{20}N_4ZnCl_4$: C, 22.02; H, 4.59; N, 12.84; Cl, 32.57. Found: C, 22.05; H, 4.68; N, 12,69; Cl, 32.37.

1,9-Diamino-4,5-dimethyl-3,7-diazanona-3-enenickel(II) Tetrachlorozincate. Tris(ethylenediamine)nickel(II) chloride dihydrate (5.5 g) is dissolved, on warming, in a mixture of ethanol (300 ml) and ethylene glycol (200 ml). Zinc chloride (5.5 g) is dissolved in 100 ml of hot ethanol and added to this solution, together with 5.5 g of redistilled 4-hydroxy-3-methyl-2-butanone. The mixture, so formed, is refluxed for 27 hr when all the violet precipitate dissolves and some orange crystals deposit. This initial product amounts to about 4.0 g and, on being fractionally crystallized from a mixture of hot methanol and ethylene glycol, using ether, yields three fractions of pure product (3.3 g). Treatment of the original filtrate with ether yields an additional 3.1 g of product; the total yield is 6.4 g (90%). The compound may be recrystallized from a hot methanol–ethylene glycol mixture containing a little ether.

Anal. Calcd for $NiC_9H_{22}N_4ZnCl_4$: C, 24.00; H, 4.99; N, 12.47; Cl, 31.56. Found: C, 24.18; H, 5.07; N, 12.53; Cl, 31.13.

2,10-Diamino-7-methyl-4,8-diazaundeca-4-enenickel(II) Tetrachlorozincate(II). This compound can be prepared by the procedure described immediately above. However, a better yield is obtained by the following procedure. Tris(1-propylenediamine)-nickel(II) tetrachlorozincate(II) (8.2 g) is suspended in ethanol (200 ml) and heated under reflux. Acetaldehyde (8 ml) in ethanol (100 ml) is added over a 2.5-hr period, and the mixture so formed is refluxed for a further 5 hr. The mixture is allowed to stand for 2 days, and the yellow crystalline material which separates is collected at the pump, washed with ethanol and then ether, and air-dried; the yield is 7.1 g (96%). This material can be purified by recrystallization from hot methanol containing ethylene glycol, by the addition of a little ether.

Anal. Calcd for $NiC_{10}H_{24}N_4ZnCl_4$: C, 25.81; H, 5.38; N, 12.04. Found: C, 25.54; H, 5.57; N, 11.40.

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Reactions of Coordinated Ligands. XVII. The Reactions between Tris(ethylenediamine)nickel(II) Ion and α-Hydroxy Ketones

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Abstract: Tris(ethylenediamine)nickel(II) salts react with α-hydroxy ketones, containing tertiary, secondary, or primary alcohol groups, to give blue, paramagnetic bis(tridentate) complexes in which the ligand is the Schiff base formed from the hydroxy ketone and ethylenediamine. The product from the reaction with the tertiary alcohol, 2-methyl-2-hydroxy-3-butanone, can be pyrolyzed and reduced to a nickel complex of trimethyltriethylenetetramine. Ethylenediamine has been replaced with 1-propylenediamine in some of these reactions.

The novel reaction between tris(ethylenediamine)-nickel(II) ion and β-hydroxycarbonyl compounds to yield compounds of type I has been shown to be quite general with respect to substitution in the organic moiety.[1] Complexes containing a ligand of this class were first prepared by condensation with acetone.[2] Closely related reactions using α,β-unsaturated ketones

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[2] D. A. House and N. F. Curtis, *ibid.*, **86**, 1331 (1964).