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.

Acknowledgment. These investigations were supported by National Science Foundation Grant GP-189. This financial assistance is deeply appreciated. We wish to thank Mr. R. Lewis and Mr. D. L. Smith for refining the syntheses of compounds III and X described in this paper.

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

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Contribution from the Evans and McPherson Chemical Laboratories,
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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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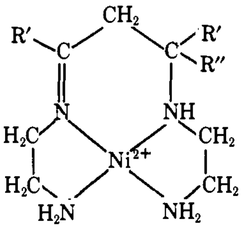
[1] T. E. MacDermott and D. H. Busch, *J. Am. Chem. Soc.*, **89**, 5780 (1967).

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

have also been reported.[1,3] Reduction of the C=N has also been carried out and the isolation[4] of the resulting long-chain substituted tetramine has been demonstrated.



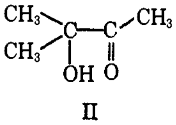
I

Extension of this system to the preparation of tetramines with different chain lengths clearly must involve using either longer chain diamines or hydroxy ketones other than the β type. An attempt has been made[1] to react tris(ethylenediamine)nickel(II) ion with the γ-hydroxy ketone, 1-hydroxy-4-pentanone, but no reaction occurs under the conditions normally used in the formation of I. When the diamine chain length is extended from ethylenediamine to trimethylenediamine, no observable reaction occurs with diacetone alcohol under conditions which give almost quantitative formation of I (R, R′, R″ = CH_3) from tris(ethylenediamine)nickel(II) and diacetone alcohol. This lack of reactivity may be related to the formation of a bis(isopropylidene) intermediate in the reaction between tris(trimethylenediamine)nickel(II) ion and acetone.[4,5] It is suggested that the formation of a square-planar species containing three heavily substituted, interlocking, six-membered rings is prevented in these cases by severe steric interaction. In the case of acetone, an alternative bis(isopropylidene) compound can, and does, form. With the β-hydroxy ketone no such alternative is possible; consequently, no reaction of this type occurs.

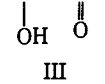
The structural variation of the systems of interest here involves the shortening of the hydroxy ketone chain, *i.e.*, the use of α-hydroxy ketones in reactions with tris(diamine)nickel(II) species. In this paper we describe the complexes of the novel ligands obtained by the reactions of α-hydroxy ketones with tris(ethylenediamine)nickel(II) salts, and some of the reactions of the products so formed. The reaction of one of these α-hydroxy ketones, 3-hydroxy-3-methyl-2-butanone, with tris(trimethylenediamine)nickel(II) ion produces a completely new type of ligand which has been reported separately.

Results and Discussion

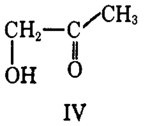
These investigations have considered the reactions between three α-hydroxy ketones and tris(ethylenediamine)nickel(II) salts. The hydroxy ketones are the tertiary alcohol, 3-hydroxy-3-methyl-2-butanone (II), the secondary alcohol, acetoin (III), and the primary alcohol, hydroxyacetone (IV).



II



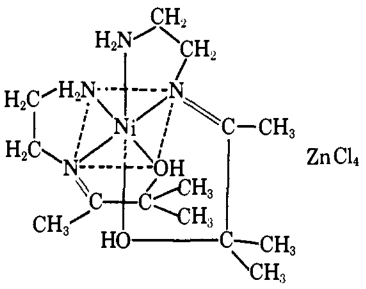
III



IV

When tris(ethylenediamine)nickel(II) chloride dihydrate is refluxed in ethanol–ethylene glycol mixed solvent, for several hours, with zinc chloride and an excess of II, the solution becomes deep blue in color. A bright blue crystalline product separates quantitatively as the solution cools. This compound gives near-infrared and visible spectra typical of octahedral nickel (λ_{max} 920 mμ (ε 10), 600 (ε 9), 360 (ε 14)). The effective magnetic moment of 2.84 BM is also consistent with the pseudo-octahedral geometry. The compound hydrolyzes in dilute acid, and steam distillation yields II from the products of hydrolysis. Elemental analyses indicate that the new compound contains two ethylenediamine and two hydroxy ketone residues associated with each nickel atom in such a way that three oxygen atoms are retained in the composition. Dehydration at 110° and 0.1 mm pressure removes exactly 1 mole of water of crystallization in 24 hr.

The infrared spectral features of this reaction product in its hydrated and dehydrated forms are most helpful. The hydrated compound has a broad shoulder centered about 3500 cm^{-1} and a fairly sharp peak at 1640 cm^{-1}. On dehydration the peak at 1640 cm^{-1} disappears and a sharp doublet (3550 and 3470 cm^{-1}) replaces the shoulder at 3500 cm^{-1}. We conclude that all the water is removed by dehydration and that the dehydrated product contains two hydroxy groups. The strong sharp singlet at 1680 cm^{-1} is assigned to the C=N stretching mode. On treatment with sodium borohydride in methanol, the compound is reduced and this peak is completely lost. Its intensity suggests that more than one double bond is present and that they are in very similar environments. The triplet at 3320, 3250, and 3170 cm^{-1}, in combination with the singlet at 1595 cm^{-1}, demonstrates the presence of NH_2 groups in the molecule. The sharp peak at 1370 cm^{-1} is associated with the *gem*-dimethyl group. In this series of compounds such a peak is always found between 1365 and 1375 cm^{-1}. From all of these considerations this blue compound has been assigned structure V. The placement of these tridentate ligands in meridional sites is indicated by an inspection of scale models. The azomethine linkage would cause severe steric strain in the formation of either "facial" isomer.



V

Further evidence for structure V comes from a study of a material isolated from the filtrate from the separation of V. This pale yellow material is precipitated as the tetraphenylborate salt. Qualitative tests reveal that nickel is absent and zinc is present. The infrared spectrum shows the presence of NH_2 (3320, 3280, 3170 cm^{-1}) and C=N (1675 cm^{-1}) groups. A sharp singlet at 3521 cm^{-1} (OH stretch), in conjunction with a sharp singlet at 1620 cm^{-1} (OH_2 deformation), is taken to indicate the presence of a coordinated water molecule.

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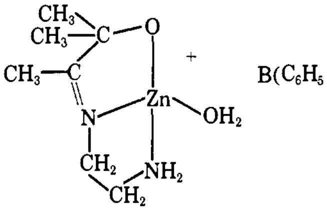
[3] N. F. Curtis and R. W. Hay, *Chem. Commun.*, 908 (1966).

[4] T. E. MacDermott, B. E. Sewall, and D. H. Busch, unpublished results.

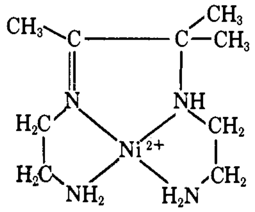
[5] D. H. House and N. F. Curtis, *J. Am. Chem. Soc.*, 86, 223 (1964).

These observations lead to the postulation of structure VI. Elemental analyses confirm this stoichiometry.



VI

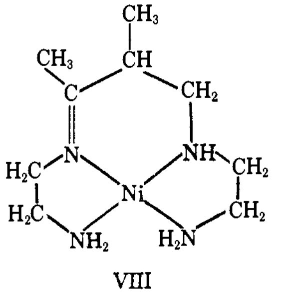
An unusual reaction occurs when V is boiled in ethylene glycol solution at atmospheric pressure. When all the solvent is boiled away this compound converts into an orange-brown tar, which on triturating with ethanol solidifies into a brown powder. On stirring this solid with cold methanol a green solution is formed and a bright yellow powder remains undissolved. This yellow compound may be crystallized from hot methanol as shining yellow plates. Its infrared spectrum indicates that the NH_2, C=N, and $C(CH_3)_2$ groups are still present. This product, in its color, diamagnetism, and infrared spectrum, very closely resembles the compounds of type I derived from β-hydroxy ketones. The double bond can be reduced by sodium borohydride in methanol, though complete reduction requires several cycles. From this evidence, this pyrolysis product has been assigned structure VII.



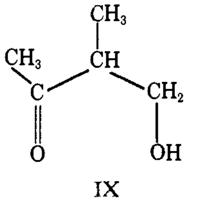
VII

The reduction described above, therefore, yields the nickel derivative of an interesting asymmetric quadridentate ligand related to triethylenetetramine. It therefore constitutes an important illustration of a new synthesis for novel asymmetric quadridentate ligands.

The isomeric species VIII is a possible product of this pyrolysis. VIII has been described[1] as a product of the reaction of tris(ethylenediamine)nickel(II) ion and IX. Comparison of the infrared spectrum of VIII



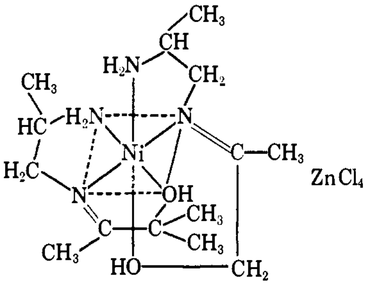
VIII



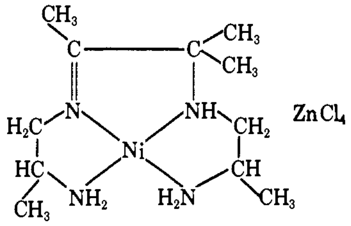
IX

with that of VII shows various differences, the most important of which is the absence in the spectrum of VIII of the peak at 1375 cm^{-1} which is assigned to the *gem*-dimethyl group in VII. Furthermore, the C=N stretching mode occurs at 1660 cm^{-1} for VII but at 1645 cm^{-1} for VIII, indicating a difference in the metal binding in the two cases. It is reasonable to expect that greater steric strain will exist in the unsaturated five-membered chelate ring (VII) than in the corresponding six-membered ring (VIII). It is concluded that VII is formed by direct replacement of the hydroxy group by an amine nitrogen and that the reaction does not proceed by prior dehydration. Dehydration would lead to VIII, which clearly is not the product of the pyrolysis of V.

Use of tris(1-propylenediamine)nickel(II) ion in parallel reactions produces X and XI. The placement



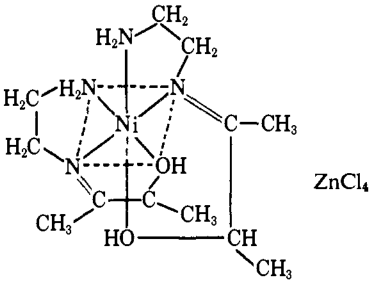
X



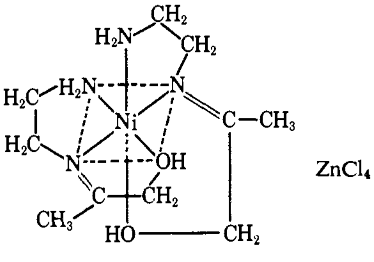
XI

of the methyl substituents on the carbon atoms next to the terminal amines is in accord with scale models which suggest that the alternative structures would involve considerably more crowding. Reduction of XI with sodium borohydride in methanol proceeds smoothly.

Compounds III and IV also react with tris(ethylenediamine)nickel(II) chloride dihydrate in the presence of zinc chloride to give blue-violet compounds which, from their similarity to V in appearance and infrared spectra and from their stoichiometries, are assigned structures XII and XIII, respectively. It is interesting to note that, while VII forms quantitatively after several hours refluxing and still remains the only product after several days, XII and XIII are only intermediates in the reactions in which they form. Both decompose in boiling methanol, XIII decomposes even at room tem-



XII



XIII

perature in the solid state. XII and XIII are not smoothly pyrolyzed by the method described for the formation of VII and XI from V and X, respectively. In neither case have the products of decomposition or pyrolysis been identified.

Experimental Section

Bis(2,3-dimethyl-6-amino-2-hydroxy-4-azahex-3-ene)nickel(II) Tetrachlorozincate(II) (V). Solutions of tris(ethylenediamine)-nickel(II) chloride dihydrate (15.0 g, 0.043 mole) in hot ethylene glycol (300 ml) and of zinc chloride (15 g) in hot methanol (200 ml) are mixed. A mauve precipitate forms. 3-Hydroxy-3-methyl-2-butanone (II) (15 g, 0.147 mole) and ethanol (550 ml) are added and the mixture is refluxed for 3 hr. By this time, the mixture is practically homogeneous and deep blue in color. A small amount of residual solid is removed by filtering and the solution is allowed to cool overnight. A small aliquot of this solution is induced to crystallize in a test tube by scratching the wall of the tube with a glass rod. These crystals are then used to seed the bulk of the solution, causing separation of the product; yield 28.9 g. Ether (800 ml) is added to the filtrate, whereupon it becomes slightly cloudy. More blue product separates (0.25 g). The total yield of crude product is about 100%. This compound is recrystallized from hot methanol to give a hydrated product, which is dehydrated by heating at 110° at reduced pressure (1.0 mm) for 24 hr.

Anal. Calcd for $NiC_{14}H_{32}N_4O_2ZnCl_4H_2O$: C, 29.47; H, 5.96; N, 9.82; H_2O, 3.16. Found: C, 29.16; H, 5.92; N, 9.72; H_2O, 3.58. Calcd for $NiC_{14}H_{32}N_4O_2ZnCl_4$: C, 30.43; H, 5.80; N, 10.14; Cl, 25.63. Found: C, 29.97; H, 6.04; N, 10.00; Cl, 25.76.

Hydrolysis of the above product is very rapid in warm acid solution. Steam distillation gives an organic hydrolysis product which is identified as the starting material, 3-hydroxy-3-methyl-2-butanone. The dinitrophenylhydrazone of this compound has a melting point of 138° as does the dinitrophenylhydrazone of the starting compound. The melting point of a mixture of the two is also 138°.

Aquo-4,5,5-trimethyl-1-amino-3-azapent-3-ene-5-hydroxylatozinc(II) Tetraphenylborate (VI). The filtrate left after isolation of bis(4,5,5-trimethyl-1-amino-3-aza-5-hydroxypent-3-ene)nickel-(II) tetrachlorozincate(II), as described above, is bright yellow. All solvents except ethylene glycol are removed on the rotary evaporator. Sodium tetraphenylborate (1 g), dissolved in 200 ml of warm water and filtered, is added to the warm ethylene glycol solution (total volume 500 ml). The pale yellow flocculent precipitate is stirred for 2 days, filtered under suction, washed with water, methanol, and ether, and dried under an infrared lamp. A second small fraction is obtained by repeating the process. The second fraction is more crystalline and may be recrystallized from hot methanol.

Anal. Calcd for $ZnC_{31}H_{37}N_2BO_2$: C, 68.50; H, 6.81; N, 5.16. Found: C, 69.12; H, 6.81; N, 5.38.

The material gives a positive test for zinc (sulfide), but no precipitate with dimethylglyoxime.

4,5,5-Trimethyl-1,8-diamine-3,6-diazaocta-3-enenickel(II) Tetrachlorozincate (VII). One gram of blue bis(4,5,5-trimethyl-1-amino-3-aza-5-hydroxypent-3-ene)nickel(II) tetrachlorozincate is dissolved by warming in 1 ml of ethylene glycol. The mixture is then heated cautiously in a test tube over a hot meeker burner until all the solvent has evaporated and the residue is brown (with a faint greenish tint). This brown gum is triturated with 10 ml of ethanol and caused to solidify. It is filtered and washed with ethanol. The crude yield is 0.7 g. This greenish yellow solid is heated with methanol (40 ml) on a hot plate for a few minutes. The undissolved yellow solid is filtered from the greenish yellow solution (yield 66%). The product is then recrystallized from hot methanol containing a few drops of ether. It is allowed to crystallize at 5° overnight, and the bright yellow plates are filtered under suction, washed with ethanol and ether, and dried under an infrared lamp.

Anal. Calcd for $NiC_9H_{22}N_4ZnCl_4$: C, 24.00; H, 4.99; N, 12.47; Cl, 31.56. Found: C, 23.85; H, 4.93; N, 12.38; Cl, 31.79.

3,6-Diaza-4,5,5-trimethyl-1,8-diaminooctanenickel(II) Tetraphenylborate. A small sample of VII prepared as described above (0.35 g, 7.8×10^{-4} mole) is dissolved in methanol (150 ml) and added to a filtered solution of sodium tetraphenylborate (0.54 g) in water (150 ml). A yellow product begins to separate, and more water is added (up to 300 ml) until no more product separates. The mixture is kept cold for 12 hr, after which time the yellow product is collected by filtration, washed with water, and dried under a heat lamp. The yield of the tetraphenylborate salt of VII is 0.51 g, 74%. Part of this product (0.45 g, 5.1×10^{-4} mole) is dissolved in hot methanol (200 ml, 50°) and sodium borohydride (0.1 g, 2.6×10^{-3} gram formula weight) is added. The color changes from yellow to lavender to gray and back to yellow. At this point three times the volume of water is added and the sides of the flask are scratched with a glass rod to initiate crystallization. The mixture is then set aside at 5° overnight to allow complete crystallization of the product. The pale yellow solid is collected by filtration, washed with water, and dried under a heat lamp (yield 0.42 g, 93%). It is necessary to repeat this reduction cycle twice, using 0.02 g of sodium borohydride each time, in order to completely reduce the C=N present (infrared evidence). After the third reduction cycle the volume of the solution has to be reduced before a product separates. The final yield is 0.21 g, 47%. The compound was dried over phosphorus pentoxide under vacuum.

Anal. Calcd for $NiC_9H_{24}N_4[B(C_6H_5)_4]_2$: C, 77.30; H, 7.29; N, 6.33; B, 2.44. Found: C, 76.94; H, 7.34; N, 6.29; B, 2.64.

Attempts to scale up the quantities used in this reduction by a factor of 10 were unsuccessful, resulting in dark colored, partially reduced products.

Bis(4,5-dimethyl-1-amino-3-aza-5-hydroxypent-3-ene)nickel(II) Tetrachlorozincate (XII). A solution of 3-hydroxy-2-butanone (1 g) in 10 ml of methanol is added to a suspension of tris(ethylenediamine)nickel(II) chloride dihydrate (2.5 g) in methanol (25 ml). The undissolved complex passes into solution on warming and stirring the mixture for a few minutes. The addition of a hot solution of zinc chloride (2.5 g) in methanol (25 ml) causes the immediate precipitation of a mauve compound identified, tentatively, by its infrared spectrum as $[Ni(en)_3][ZnCl_4]$. The yield of this compound is 1.45 g. The blue filtrate remaining is treated with ether until the onset of clouding. Crystallization is induced by scratching the sides of the flask with a glass rod, and the solution is then set aside. A crystalline product (1.8 g) is thus obtained and subsequent fractions bring the total yield up to 2.1 g. This material is very similar in appearance to V. Its infrared spectrum is also extremely similar. It is recrystallized from hot methanol containing a little ether.

Anal. Calcd for $NiC_{12}H_{28}N_4O_2ZnCl_4$: C, 27.48; H, 5.34; N, 10.69; Cl, 27.10. Found: C, 27.17; H, 5.41; N, 10.75; Cl, 26.97.

Bis(4-methyl-1-amino-3-aza-5-hydroxypent-3-ene)nickel(II) Tetrachlorozincate (XIII). One gram of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ is dissolved in the minimum amount of warm methanol and 2 g of 40% hydroxyacetone (IV) is added. Five minutes after mixing, the purple solution turns blue. Zinc chloride (1 g) in a minimum volume of hot methanol is added and the immediate mauve precipitate of $[Ni(en)_3][ZnCl_4]$ is removed by filtering (0.4 g). Ether is added to the blue filtrate and an oil separates. The oil crystallizes when the vessel wall is rubbed with a glass rod. The product is collected and washed with a 50:50 methanol–ether mixture, followed by pure ether. The yield is 0.7 g. The compound is recrystallized from a mixture of methanol and ether. The infrared spectrum of the product is very similar to that of V.

Anal. Calcd for $NiC_{10}H_{24}N_4O_2ZnCl_4$: C, 24.19; H, 4.84; N, 11.29; Cl, 28.63. Found: C, 24.12; H, 4.84; N, 11.13; Cl, 28.71.

Bis(2,3-dimethyl-6-amino-2-hydroxy-4-azahept-3-ene)nickel(II) Tetrachlorozincate and 4,7-Diaza-5,6,6-trimethyl-2,9-diaminodeca-4-enenickel(II) Tetrachlorozincate. These compounds were prepared by procedures closely related to those used for V and VII, respectively. Products were identified by infrared spectra.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged.