

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VICTORIA UNIVERSITY OF WELLINGTON, WELLINGTON, NEW ZEALAND]

Transition Metal Complexes with Aliphatic Schiff Bases. VI. Compounds Formed by the Reaction of Copper(II) and Nickel(II) Ethylenediamine and Triethylenetetramine Complexes with Some Aliphatic Aldehydes¹

BY D. A. HOUSE AND N. F. CURTIS

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$\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ (trien = triethylenetetramine) reacts with propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde to form orange diamagnetic nickel(II) complexes of cyclic tetradentate ligands with one azomethine and three secondary amine donor groups. A similar reaction occurs between $\text{Ni}(\text{en})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Cu}(\text{en})_2\text{Cl}_2$ (en = ethylenediamine) and the aldehydes, forming complexes of linear tetradentate ligands with one azomethine, one secondary amine, and two primary amine donor groups. These compounds are analogous to previously reported compounds formed by condensation of the amine complexes with acetone. Visible and ultraviolet spectra and magnetic susceptibilities are reported for these new complexes.

Compounds prepared by the reaction of some aliphatic ketones with polyamine ligands coordinated to Cu(II) and Ni(II) have been previously described.²⁻⁷ This paper describes analogous compounds prepared by reaction of propionaldehyde and *n*- and isobutyraldehyde with the Cu(II) and Ni(II) complexes of ethylenediamine and with the Ni(II) complexes of triethylenetetramine.

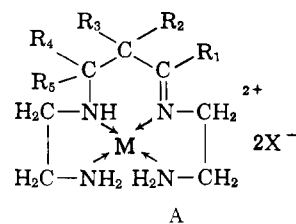
Ethylenediamine Derivatives.—When a methanol solution of $\text{Ni}(\text{en})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , and one of the aldehydes is heated in a sealed tube, reaction occurs and the tube wall becomes coated with yellow crystals of the tetrachlorozincate salt of a tetradentate Ni(II) complex (A), which has one secondary amine, one azomethine, and two primary amine donor groups. A similar reaction occurs with acetone, and the tetrachlorozincate salt isolated is analogous to the perchlorate previously described.^{2,7}

Reaction of $\text{Ni}(\text{en})_2(\text{ClO}_4)_2$ with acetone produces compounds with two (type A) or three acetone residues.^{2,7} (The latter formed from type A by condensation of an *N*-isopropylidene group on one of the primary amine groups.) Further reaction with acetone, to form the cyclic tetradentate complex (B), occurs only in the presence of diamine catalyst, as when $[\text{Ni}(\text{en})_3]^{2+}$ reacts with acetone.⁸ In the presence of ZnCl_2 the reaction of $[\text{Ni}(\text{en})_3]^{2+}$ stops at the A stage. This is attributed to the removal by the ZnCl_2 of the catalytic third mole of ethylenediamine, and also to the crystallization, as formed, of product A as the acetone-insoluble tetrachlorozincate. Attempts to form analogs of B by reaction of $\text{Ni}(\text{en})_3(\text{ClO}_4)_2$ with the aldehydes in the absence of ZnCl_2 were not successful, probably because of a slower reaction rate for the formation of the second bridge. For comparison, complete reaction of $\text{Ni}(\text{en})_3(\text{ClO}_4)_2$ with methyl ethyl ketone to form the A analog occurs in several hours at 100°, while the yield of the B analog was less than 10% after 2 months at 140°. Reactions as slow as this would not be observed with aldehydes because of faster competing polymerization reactions.

The addition of ZnCl_2 to the reaction mixture facili-

tates isolation of the compounds as the tetrachlorozincate salts, since salts with other common anions, including perchlorate, tend to be very soluble. ZnCl_2 often acts as a catalyst for Schiff base condensations, but for these reactions it has not been shown to have any catalytic effect, other than that attributable to dehydrating agents in general. The ZnCl_2 also removes the released mole of ethylenediamine, which would otherwise cause base-catalyzed polymerization of the aldehyde.

The corresponding Cu(II) complexes are prepared by refluxing a methanol solution of $\text{Cu}(\text{en})_2\text{Cl}_2$ with the aldehyde (or acetone) and adding the resulting solution to a methanol solution of ZnCl_2 when the tetrachlorozincate salt crystallizes. The corresponding perchlorate salts are prepared by adding the reacted chloride solution to a saturated aqueous solution of NaClO_4 .



From propionaldehyde

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$,
 $\text{R}_3 = \text{CH}_3$, $\text{R}_5 = \text{CH}_3\text{CH}_2$ —
 I, M = Ni; X = $\frac{1}{2}\text{ZnCl}_4$
 II, M = Cu; X = $\frac{1}{2}\text{ZnCl}_4$
 III, M = Cu; X = ClO_4

From *n*-butyraldehyde

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$,
 $\text{R}_3 = \text{CH}_3\text{CH}_2$, $\text{R}_5 = \text{CH}_3\text{CH}_2\text{CH}_2$ —
 IV, M = Ni; X = $\frac{1}{2}\text{ZnCl}_4$
 V, M = Cu; X = $\frac{1}{2}\text{ZnCl}_4$
 VI, M = Cu; X = ClO_4

From isobutyraldehyde

$\text{R}_1 = \text{R}_4 = \text{H}$,
 $\text{R}_2 = \text{R}_3 = \text{CH}_3$, $\text{R}_5 = (\text{CH}_3)_2\text{CH}$ —
 VII, M = Ni; X = $\frac{1}{2}\text{ZnCl}_4$
 VIII, M = Cu; X = $\frac{1}{2}\text{ZnCl}_4$
 IX, M = Cu; X = ClO_4

From acetone

$\text{R}_1 = \text{R}_4 = \text{R}_5 = \text{CH}_3$,
 $\text{R}_2 = \text{R}_3 = \text{H}$
 X, M = Ni; X = $\frac{1}{2}\text{ZnCl}_4$
 XI,² M = Ni; X = ClO_4
 XII, M = Cu; X = $\frac{1}{2}\text{ZnCl}_4$
 XIII,⁴ M = Cu; X = ClO_4

(1) Presented at the pre-A.N.Z.A.A.S. symposium on Coordination Chemistry, Sydney, Australia, Aug., 1962.

(2) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).

(3) M. M. Blight and N. F. Curtis, *ibid.*, 1204 (1962).

(4) M. M. Blight and N. F. Curtis, *ibid.*, 3016 (1962).

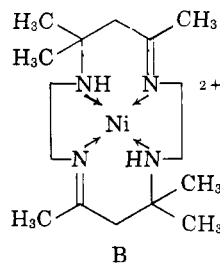
(5) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962).

(6) D. A. House and N. F. Curtis, *ibid.*, **86**, 223 (1964).

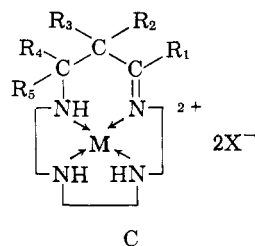
(7) N. F. Curtis and D. A. House, *Chem. Ind. (London)*, **42**, 1708 (1961).

(8) H. K. G. Powell, Thesis, University of New Zealand, 1960.

(9) M. M. Blight, Thesis, University of New Zealand, 1957.



Triethylenetetramine Derivatives.—In the presence of ZnCl_2 , $\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ reacts with the aldehydes to give cyclic tetradentate complexes (C), which have three secondary amine and one azomethine donor groups. $\text{Cu}(\text{trien})\text{Cl}_2 \cdot n\text{H}_2\text{O}$ and ZnCl_2 readily form methanol-insoluble $\text{Cu}(\text{trien})\text{ZnCl}_4^{10}$ and no reaction occurs with the added aldehyde. Attempted reaction of $\text{Cu}(\text{trien})\text{Cl}_2 \cdot n\text{H}_2\text{O}$ with aldehydes in the presence of CaSO_4 as a dehydrating agent led to extensive reduction of the $\text{Cu}(\text{II})$ complex (*cf.* Fehling's solution as a reagent for aldehydes).



From propionaldehyde

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$,
 $\text{R}_3 = \text{CH}_3$, $\text{R}_5 = \text{CH}_3\text{CH}_2$ —
 XIV, $\text{M} = \text{Ni}$; $\text{X} = \frac{1}{2}\text{ZnCl}_4$

From *n*-butyraldehyde

$\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$,
 $\text{R}_3 = \text{CH}_3\text{CH}_2$, $\text{R}_5 = \text{CH}_3\text{CH}_2\text{CH}_2$ —
 XV, $\text{M} = \text{Ni}$; $\text{X} = \frac{1}{2}\text{ZnCl}_4$

From isobutyraldehyde

$\text{R}_1 = \text{R}_4 = \text{R}_5 = \text{H}$,
 $\text{R}_2 = \text{R}_3 = \text{CH}_3$ —
 XVI, $\text{M} = \text{Ni}$; $\text{X} = \frac{1}{2}\text{ZnCl}_4$

From acetone

$\text{R}_1 = \text{R}_4 = \text{R}_5 = \text{CH}_3$,
 $\text{R}_2 = \text{R}_3 = \text{H}$
 XVII, $\text{M} = \text{Ni}$; $\text{X} = \frac{1}{2}\text{ZnCl}_4$
 XVIII, $\text{M} = \text{Cu}$; $\text{X} = \frac{1}{2}\text{ZnCl}_4$
 XIX, $\text{M} = \text{Cu}$; $\text{X} = \text{ClO}_4$

Structure and Chemical Properties.—The method of preparation and the chemical and physical properties of the compounds indicate that they are analogous to the previously described compounds formed by reaction of $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ ethylenediamine and triethylenetetramine complexes with acetone. The $\text{Ni}(\text{II})$ compounds are diamagnetic indicating a square-planar four-coordinate structure. The infrared spectra of all the compounds show a strong band near 1665 cm^{-1} , attributed to the $\text{C}:\text{N}$ group, and a band near 3150 cm^{-1} , attributed to the coordinated NH group. In the case of the triethylenetetramine derivative, bands in the infrared spectrum of the starting material near 3330 and 1595 cm^{-1} , attributed to the stretching and deformation of the coordinated NH_2 groups, are absent after reaction with the carbonyl compounds, supporting the cyclic Schiff base-secondary amine structure (C).

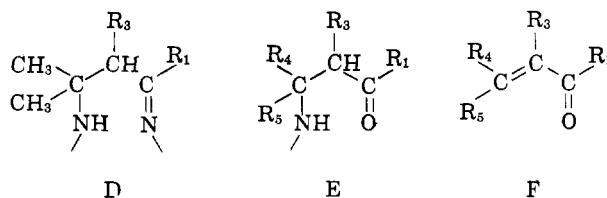
(10) D. A. House and N. F. Curtis, *J. Chem. Soc.*, 3149 (1963).

The resistance to chemical attack of these compounds is similar to that of the analogs derived from acetone. The noncyclic complexes (A) derived from ethylenediamine are decomposed slowly by dilute mineral acids, and very slowly by dilute acetic acid and by reagents such as cyanide, sulfide, or ammoniacal dimethylglyoxime. The cyclic tetradentate complexes (C) derived from triethylenetetramine are not decomposed by concentrated acids or alkalies, or by the reagents listed above, but are attacked by powerful oxidizing agents (such as acid permanganate or boiling peroxydisulfate solutions) and by solutions containing cyanide ions.

When the solution resulting from decomposition of the compounds (by acid for A and cyanide for C) was steam distilled, α,β -unsaturated carbonyl compounds, obtained by condensation of 2 moles of the carbonyl compound used in the original synthesis, were isolated from the distillate. Thus, complexes formed from propionaldehyde gave α -methyl- β -ethyl acrolien, those from *n*-butyraldehyde gave α -ethyl- β -propyl acrolien, and those from acetone gave mesityl oxide.⁷ (The compounds derived from isobutyraldehyde were exceptional, as described below.) These carbonyl compounds were isolated from the steam distillate by precipitation as the 2,4-dinitrophenylhydrazine derivative and characterized by comparison of the X-ray powder pattern^{11,12} with that of the α,β -unsaturated carbonyl derivative prepared by conventional techniques.^{13,14}

Decomposition of the C compounds by cyanide probably occurs through removal of the metal ion as the cyano complex, leaving the noncoordinated Schiff base (D). Aliphatic Schiff base compounds are readily hydrolyzed, in this case yielding a β -amino ketone (E), also readily hydrolyzed¹⁵ to form an amine and the α,β -unsaturated carbonyl compound (F) obtained by condensation of 2 moles of the original carbonyl compound, as observed. Acid hydrolysis of the A compounds follows the same pattern.

The isolation of the α,β -unsaturated carbonyl compounds observed supports the proposed structures, with C_3 bridges linking the amine residues.



The complexes formed from isobutyraldehyde and the nickel(II) or copper(II) ethylenediamine complexes gave only isobutyraldehyde on decomposition. This is not surprising as an α,β -unsaturated aldehyde cannot be formed from the bridging unit involved in the isobutyraldehyde complexes because there is no α -hydrogen for amine elimination and double bond formation.¹⁶⁻¹⁸ Elimination could take place to give

(11) G. L. Clark, W. I. Kaye, and T. D. Parks, *Anal. Chem.*, **18**, 310 (1946).

(12) B. E. Gordon, F. Wopat, H. D. Burnham, and L. C. Jones, *ibid.*, **23**, 1754 (1951).

(13) O. Doebner, *Ber.*, **35**, 1144 (1902).

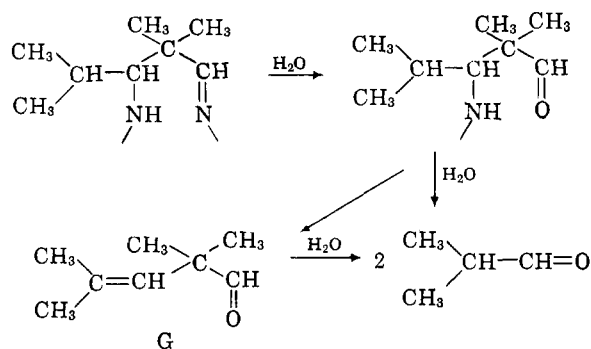
(14) C. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

(15) N. H. Cromwell, *Chem. Rev.*, **38**, 124 (1946).

(16) V. Grignard and Th. N. Iliesco, *Compt. rend.*, **190**, 556 (1930).

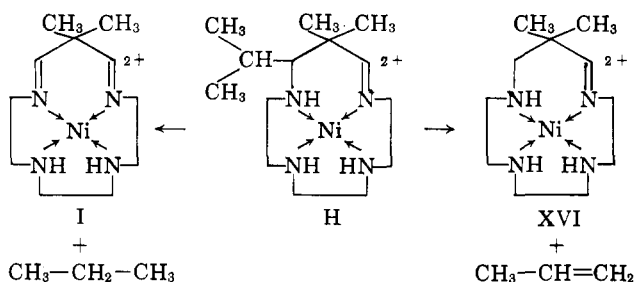
(17) R. H. Saunders, M. J. Murray, and F. F. Cleveland, *J. Am. Chem. Soc.*, **65**, 1714 (1943).

the nonconjugated unsaturated aldehyde, α,α -dimethyl- β -isopropylidene acrolien (G), but this is reported to be readily hydrolyzed to isobutyraldehyde.¹⁶



Compound VII, formed by reaction of isobutyraldehyde with $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, is analogous to those formed with other aldehydes and ketones. Analytical data for XVI, formed by reaction of isobutyraldehyde with $\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, indicate a structure with three fewer carbon atoms than expected. XVI shows the same chemical stability as the other three carbon bridge cyclic complexes derived from triethylenetetramine and a similar structure seems likely. Steam distillation of the cyanide ion decomposition products gave isobutyraldehyde as the only identified carbonyl compound. XVI probably arises from the hypothetical initial product (H) by elimination of propene. Elimination of propane to give I with two C:N groups is excluded since hydrogen uptake (with platinum catalyst at atmospheric pressure at room temperature) ceased after absorption of 1 mole (H_2),¹⁹ and the infrared spectrum of the isolated reduction product showed no CN absorption at 1665 cm^{-1} .

Electronic Absorption Spectra and Magnetic Properties.—The ultraviolet and visible absorption maxima in aqueous solution are given in Table I. The positions, intensities, and assignments are similar to those for



analogous complexes described previously.²⁻⁶

The magnetic susceptibilities were measured for the solids by the Gouy method using $\text{Ni(en)}_3\text{S}_2\text{O}_3$ as calibrant.²⁰ The nickel(II) compounds measured were diamagnetic (VII, XV, XVI, and XVII) and the values for the copper(II) compounds (Table II) all indicate the presence of one unpaired electron.

Experimental

The chemicals used were of reagent grade purity and the aldehydes were freshly distilled prior to use. Acetone was dried over CaSO_4 . $\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was prepared as described pre-

(18) E. H. Usherwood, *J. Chem. Soc.*, **123**, 1717 (1923).

(19) The hydrogenation measurement and the isolation of the reduced species were done by G. A. Gordon of this department.

(20) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

TABLE I
ELECTRONIC ABSORPTION SPECTRA

Compound	Absorption maxima—		ϵ
	$m\mu$	$\text{cm}^{-1} \times 10^{-3}$	
XIV	418	23.95	115
	273	36.7	1,290
	218	46.0	11,500
XV	417	24.0	106
	283	36.3	1,700
	218	46.0	12,600
XVI	420	23.8	112
	273	36.7	1,820
	215	46.5	14,200
I	427	23.4	44
	274	36.5	720
	203	49.4	9,250
IV	427	23.4	51
	275	36.4	870
	203	49.4	13,900
VII	428	23.35	74
	276	36.7	850
	209	47.9	13,500
X	434	32.1	65
	266	37.6	1,470
	206	49.1	15,100
XIV	537	18.6	186
	264	37.8	5,980
	194	51.0	23,000
II	525	19.05	82
	238	42.0	3,870
V	521	19.2	81
	240	41.6	4,470
VIII	524	19.1	94
	255	39.35	3,120
XII	530	19.37	88
	244	40.9	4,350

TABLE II
MAGNETIC SUSCEPTIBILITIES

Compound	Mol. wt.	Temp., °K.	$\chi_g \times 10^6$	$\chi_d \times 10^6$	$\chi_{cor} \times 10^6$	μ_{eff} , B.M. ^a
XVIII	497	293	2.78	307	1677	1.99
II	471	292	2.41	293	1429	1.84
V	499	294	2.29	317	1458	1.86
VIII	499	294	2.31	317	1472	1.87

^a Calculated assuming the Curie law.

viously.^{5,8,21} The metal ion complexes were recrystallized before reacting with the carbonyl compounds.

5-Methyl-6-ethyl-1,9-diamine-3,7-diazanona-3-enenickel(II) Tetrachlorozincate(II) (I).—Anhydrous ZnCl_2 (6 g.) was dissolved in dry methanol (50 ml.) and the solution added to powdered $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6 g.) in a 100-ml. Carius tube. Freshly distilled propionaldehyde (6 ml.) was then added and the tube sealed. When heated at 100° , the solution rapidly turned yellow-orange and a small amount of (presumably) Zn(OH)_2 formed. After 30 min., orange crystals of the product appeared and after 3 hr. the tube was cooled to room temperature and finally kept for 2 hr. in ice. The crude product was collected by filtration and boiled with 25 ml. water and 1 g. of decolorizing charcoal. After filtration of the hot solution, ethanol (25 ml.) was added to the warm filtrate. Orange crystals of the ZnCl_4^{2-} salt (yield 70–80%) were obtained on cooling and were recrystallized from water-alcohol solution.

Anal. Calcd. for $\text{NiC}_{10}\text{H}_{24}\text{ZnCl}_4$: Ni, 12.6; C, 25.8; H, 5.2; Cl, 30.4. Found: Ni, 12.8; C, 25.7; H, 5.6; Cl, 30.6.

5-Ethyl-6-propyl-1,9-diamine-3,7-diazanona-3-enenickel(II) Tetrachlorozincate(II) (IV).—Similar conditions and amounts

(21) H. B. Jonassen and B. E. Douglas, *J. Am. Chem. Soc.*, **71**, 4094 (1949).

were used as in the synthesis of I except that 6 ml. of *n*-butyraldehyde was used in place of the propionaldehyde. Yellow-orange crystals of the ZnCl_4^{2-} salt were obtained in a 70% yield.

Anal. Calcd. for $\text{NiC}_{12}\text{H}_{28}\text{N}_4\text{ZnCl}_4$: Ni, 11.9; C, 29.3; H, 5.7; Cl, 28.6. Found: Ni, 12.1; C, 29.3; H, 5.9; Cl, 28.4.

5,5-Dimethyl-6-isopropyl-1,9-diamine-3,7-diaza-3-enenickel(II) Tetrachlorozincate(II) (VII).—Similar conditions and amounts were used as in the synthesis of I except that 6 ml. of isobutyraldehyde was used in place of the propionaldehyde. Yellow crystals of the ZnCl_4^{2-} salt were obtained in an 80% yield.

Anal. Calcd. for $\text{NiC}_{12}\text{H}_{28}\text{N}_4\text{ZnCl}_4$: Ni, 11.4; C, 29.3; H, 5.7; Cl, 28.6. Found: Ni, 12.1; C, 29.2; H, 5.1; Cl, 28.6.

4,6,6-Trimethyl-1,9-diamine-3,7-diaza-3-enenickel(II) Tetrachlorozincate(II) (X).—Dry acetone (30 ml.) was added to $\text{Ni(en)}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (6 g.) in a 100-ml. Carius tube. Anhydrous ZnCl_2 (6 g.) was dissolved in dry acetone (40 ml.) and the clear solution added to the tube contents. The color of the reaction mixture changed from mauve, through blue and green, to yellow. The tube was sealed and heated at 100° for 3 hr. during which time orange crystals of the product crystallized on the walls. This crystalline material was collected by filtration and recrystallized once from the minimum amount of hot water, yield 80%.

Anal. Calcd. for $\text{NiC}_{10}\text{H}_{24}\text{N}_4\text{ZnCl}_4$: Ni, 12.6; C, 25.8; H, 5.2; Cl, 30.4. Found: Ni, 12.6; C, 25.8; H, 5.2; Cl, 30.3.

3-Methyl-4-ethyl-1,5,8,11-tetraazacyclotrideca-1-enenickel(II) Tetrachlorozincate(II) (XIV).—Anhydrous ZnCl_2 (6 g.) was dissolved in dry methanol (30 ml.) and the solution added to powdered $\text{Ni}_2(\text{trien})_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ (5 g.) in a 100-ml. Carius tube. Freshly distilled propionaldehyde (10 ml.) was then added. The tube was heated at 120° for 48 hr., cooled to room temperature, and the contents evaporated to a thick orange gum. Water (50 ml.) was added and the solution boiled several times with fresh amounts of decolorizing charcoal to remove the aldehyde polymers. A clear yellow solution was finally obtained. This was made slightly acid (litmus) with dilute HCl and set aside for slow evaporation. Orange crystals of the ZnCl_4^{2-} salt formed as needles, yield 5–10%.

Anal. Calcd. for $\text{NiC}_{12}\text{H}_{28}\text{N}_4\text{ZnCl}_4$: Ni, 11.9; C, 29.3; H, 5.3; Cl, 28.8. Found: Ni, 11.8; C, 29.6; H, 5.5; Cl, 28.9.

3-Ethyl-4-propyl-1,5,8,11-tetraazacyclotrideca-1-enenickel(II) Tetrachlorozincate(II) (XV).—Similar conditions and

amounts were used as in the synthesis of XIV except that 10 ml. of *n*-butyraldehyde were used instead of the propionaldehyde. Orange crystals of the ZnCl_4^{2-} salt were obtained in a 50% yield.

Anal. Calcd. for $\text{NiC}_{14}\text{H}_{30}\text{N}_4\text{ZnCl}_4$: Ni, 11.3; C, 32.4; H, 5.8; Cl, 27.2. Found: Ni, 11.3; C, 32.1; H, 5.9; Cl, 27.3.

3,3-Dimethyl-1,5,8,11-tetraazacyclotrideca-1-enenickel(II) Tetrachlorozincate(II) (XVI).—Similar conditions and amounts were used as in the synthesis of XIV except that 10 ml. of isobutyraldehyde were used instead of the propionaldehyde and the heating was continued for 5 days. Yellow crystals of the ZnCl_4^{2-} salt were obtained in a 50% yield.

Anal. Calcd. for $\text{NiC}_{11}\text{H}_{24}\text{N}_4\text{ZnCl}_4$: Ni, 12.3; C, 27.7; H, 5.1; Cl, 29.6. Found: Ni, 12.1; C, 27.9; H, 5.2; Cl, 29.6.

2,4,4-Trimethyl-1,5,8,11-tetraazacyclotrideca-1-enecopper(II) Perchlorate Monohydrate (XIV).— $\text{Cu}(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ (dried over concentrated sulfuric acid (39 g., 0.1 mole) was dissolved in dry acetone (300 ml.), and triethylenetetramine (14.6 g., 0.1 mole), diluted with an equal volume of dry acetone, was added slowly. The blue solution was allowed to stand in a stoppered flask at room temperature for about 2 weeks. The acetone was then allowed to evaporate slowly and a blue-purple semicrystalline solid formed. This was dissolved in the minimum amount of boiling water and filtered, and isopropyl alcohol was added to the hot filtrate. On cooling, the bright blue monohydrate perchlorate (30 g., 60%) was deposited from the maroon-colored solution.

Anal. Calcd. for $\text{CuC}_{12}\text{H}_{28}\text{N}_4\text{Cl}_2\text{O}_9$: Cu, 12.5; C, 28.5; H, 5.6; N, 11.0. Found: Cu, 12.5; C, 28.9; H, 6.0; N, 11.2.

Analyses.—The methods used were similar to those described previously.⁵

Spectra.—The visible and ultraviolet spectra were determined in aqueous solution using a Unicam S.P. 700 recording spectrophotometer. The infrared spectra were determined in mulls, a Perkin-Elmer Model 221 spectrophotometer being used.

Acknowledgments.—The authors wish to thank Mr. R. Woods of this department for the infrared spectral determinations, Dr. A. D. Campbell of the University of Otago for the carbon, hydrogen, and nitrogen analyses, and Mr. G. J. Gordon for the results from the hydrogenation of XVI.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

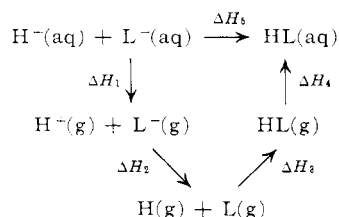
The Use of Basicity and Oxidative Coupling Potential to Obtain Group Electronegativity

BY DARL H. MCDANIEL AND AUSTIN YINGST

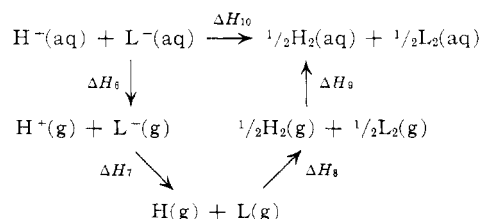
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A relationship between basicity, e.m.f. values of oxidative coupling reactions, and Pauling electronegativity values is developed. This relationship provides a vantage point for the interpretation of the Edwards double basicity scale. Use is made of the relationship to calculate a set of group electronegativities.

Thermochemical Analysis.—The factors involved in the dissociation of an acid and in the oxidative coupling of its conjugate base may be analyzed in terms of enthalpy or free energy cycles. In such an analysis similar terms arise in both the dissociation process for the general acid HL and in the oxidative coupling process for L^- producing L_2 , as may be noted by inspection of the enthalpy cycles below. For the acid HL the following cycle may be written



Similarly a cycle may be written for the oxidative coupling of the anion L^-



The steps involving hydrogen are conventionally omitted in the second cycle, but are included here for clarity in comparing oxidative coupling and acidity. From the above cycles one obtains eq. 1 and 2

$$\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \quad (1)$$

$$\Delta H_{10} = \Delta H_6 + \Delta H_7 + \Delta H_8 + \Delta H_9 \quad (2)$$

Noting that $\Delta H_1 = \Delta H_6$ and $\Delta H_2 = \Delta H_7$, subtraction of eq. 2 from eq. 1 gives eq. 3.

$$\Delta H_5 - \Delta H_{10} = \Delta H_3 - \Delta H_8 + \Delta H_4 - \Delta H_9 \quad (3)$$