[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTINGHOUSE RESEARCH LABORATORIES]

Copper (II) and Nickel (II) *N*-(*n*-alkyl)salicylaldimine Chelates

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A number of copper and nickel salicylaldimine chelates derived from straight chain primary amines have been prepared. Melting point *vs.* chain length plots are presented and comparisons made between the two series of compounds. Copper and nickel chelates of this type are suggested as suitable derivatives for characterizing primary amines. Nickel chelates of the type studied are characteristically higher melting than are the corresponding copper compounds.

A number of chelates of the general type I have been reported in the literature.[1] Of the compounds I where R is a simple straight chain hydrocarbon group, however, only the parent methyl compounds appear to have been prepared.[2,3] This paper describes the preparation of two series of chelates I where R is varied from methyl to *n*-tetradecyl. These compounds have been prepared by adaptations of conventional methods[2] involving first the condensation of salicylaldehyde with the appropriate primary amine (RNH_2), followed by reaction with a copper or nickel salt in the presence of a base. The compounds are obtained in good yields and are readily purified by recrystallization.

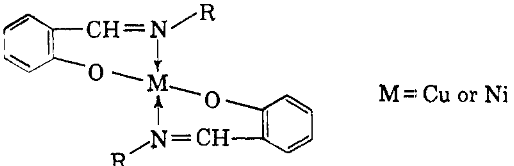

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TABLE I

COPPER CHELATES OF *N*-(*n*-ALKYL)SALICYLALDIMINE CHELATES (I, M = CU)

R	Prep. Procedure	M.P., °C	% Copper Calcd.	% Copper Found	Appearance
Methyl	A	158.5–159.0[a]	19.15	19.13	Green needles
Ethyl[b]	A	151.7–151.9	17.65	17.65	Dark green plates
n-Propyl	A	123.0–123.6	16.38	16.30	Short dark green needles
n-Butyl[c]	B	80.5– 81.0	15.27	15.20	Dark green plates
n-Amyl[d]	C	96.2– 96.8	14.28	14.14	Brown-green needles
n-Hexyl	C	83.8– 84.4	13.46	13.52	Dark green plates
n-Heptyl	C	80.0– 80.5	12.70	12.61	Brown-green needles
n-Octyl[e]	C	66.0– 66.4	12.03	12.14	Brown plates
n-Decyl	C	61.2– 62.0	10.87	10.78	Light brown plates
n-Dodecyl[f]	C	67.3– 67.6	9.92	9.94	Short brown needles
n-Tetradecyl	C	56.5– 58.0	9.12	9.13	Greenish brown microcrystalline powder

[a] Reported: 158°.[2] [b] % N: Calcd. 7.79; Found 7.58. [c] Molecular weight: Calcd. 416.0; Found 423. [d] Molecular weight: Calcd. 445.1; Found 419. % N: Calcd. 6.32; Found 6.30. [e] Molecular weight: Calcd. 528.2; Found 524. [f] % N: Calcd. 4.35; Found 4.34.

All the chelates obtained are strongly colored green or brown solids. Except for the highest members of the series, all are beautifully crystalline. All the compounds studied are moderately soluble in organic solvents and insoluble in water. It was observed that, in methyl alcohol, the copper chelates are appreciably more soluble than are the corresponding nickel chelates.

The compositions and properties of the copper chelates are listed in Table I and of the nickel chelates in Table II. In every case the compound corresponds in composition to unsolvated I. Molecular weights of several of the copper and nickel chelates were determined in freezing dioxane. All of the compounds were found to be monomeric in this solvent.

In Figure 1 the melting points of the copper and nickel chelates are plotted as a function of chain length for R. The curves obtained for the two series of chelates are very similar in appearance. In each curve a rise in melting point occurs from butyl to amyl and from decyl to dodecyl. Otherwise the melting point decreases with increasing chain length for both series. In each case the melting point of the nickel chelate is higher than that of the corresponding copper chelate. This fact suggests that intermolecular forces are characteristically greater for nickel chelates of this type than for the analogous copper compounds. This conclusion is also in agreement with the greater solubilities found for the copper chelates in methanol.

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(1) A. Martell and M. Calvin, *Chemistry of the Metal Chelates Compounds*, Prentice-Hall, Inc., New York, 1952.

(2) P. Pfeiffer and H. Glaser, *J. prakt. Chem.*, **153**, 270 (1939).

(3) V. Klemm and K. Raddatz, *Z. anorg. u. allgem. Chem.*, **250**, 207 (1942).

TABLE II

NICKEL CHELATES OF N-(n-ALKYL)SALICYLALDIMINE CHELATES (I, M = Ni)

R	Prep. Procedure	M.P., °C	% Nickel Calcd.	% Nickel Found	Appearance
Methyl	A	206.2–207.2	17.95	17.96	Mixture of green needles and plates[a]
Ethyl	B	177.2–177.6	16.53	16.33	Very dark green plates
n-Propyl[b]	A	164.8–165.6	15.32	14.80	Very dark green plates
n-Butyl[c]	B	141.8–142.4	14.27	14.03	Brownish green plates
n-Amyl[d]	C	146.7–147.5	13.36	13.20	Fine green needles
n-Hexyl	B	122.3–123.4	12.56	12.46	Green needles
n-Heptyl	C	121.4–121.6	11.85	11.90	Fine green needles
n-Octyl[e]	C	100.5–101.0	11.21	11.13	Brown needles
n-Decyl	C	89.4– 90.7	10.13	10.17	Small green plates
n-Dodecyl[f]	C	98.6– 98.8	9.23	9.42	Green microcrystalline powder
n-Tetradecyl	C	87.0– 88.5	8.49	8.57	Green microcrystalline powder

[a] This was the only compound studied which appears to exist in more than one crystalline form. [b] % N: Calcd. 7.32; Found 7.28. [c] Molecular weight: Calcd. 411.2; Found 417. [d] Molecular weight: Calcd. 440.2; Found 473. % N: Calcd. 6.38; Found 6.27. [e] Molecular weight: Calcd. 523.4; Found 567. [f] % N: Calcd. 4.41; Found 4.21.

The ease of preparation and purification of the salicylaldimine chelates, together with their sharp and convenient melting points, suggest the use of these compounds for the characterization of primary amines.[4] In the case of those amines whose chelate derivatives have similar melting points, identification is still possible, by means of mixed melting points. Melting points were determined on mixtures of several pairs of compounds from both the copper and nickel series. In all cases definite melting point depressions were observed.

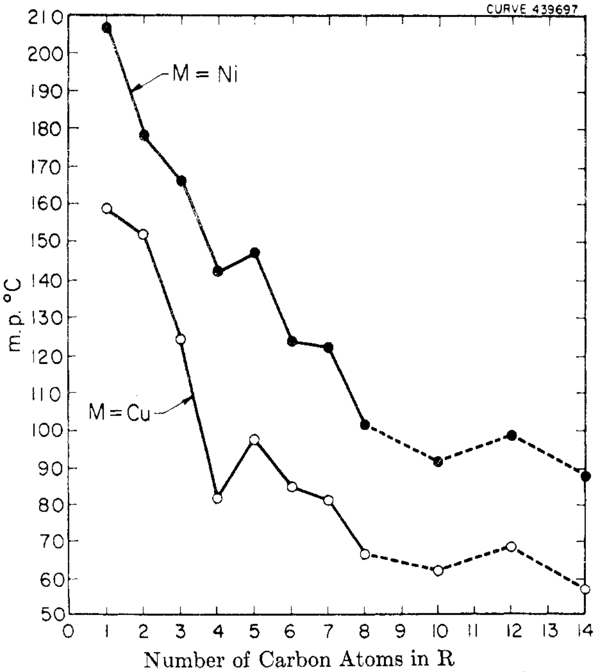
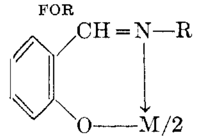


FIG. 1.—MELTING POINT AS A FUNCTION OF CHAIN LENGTH FOR



EXPERIMENTAL

Preparation of compounds. The chelates were prepared by adaptations of existing methods.[2] One of the three methods below was used in each case as indicated in Tables I and II. The initially formed Schiff base compounds were not isolated but were reacted directly in solution, with the metal salt, to form the Schiff base chelates.

Method A. To 6.1 g. (0.05 mole) of salicylaldehyde dissolved in 100 ml. of methyl alcohol was added 0.1 mole (2 fold excess) of the primary amine (either as the pure compound or as a 25% solution in water) and the mixture allowed to stand a few minutes at room temperature. A solution of 0.025 mole of copper or nickel acetate in 100 ml. of distilled water was added followed by a solution of 5 g. of sodium acetate trihydrate in 50 ml. of water. The mixture was heated nearly to boiling and stirred for 15 to 30 min. The mixture was allowed to stand at room temperature for 1 hr., or overnight, and the solid chelate filtered off on a Buchner funnel. The compound was air dried and recrystallized from methanol. The recrystallized compound was dried at room temperature *in vacuo* over $CaCl_2$. One recrystallization gave an analytically pure product in all cases. Yields of the unrecrystallized products were generally above 90%.

Method B. The procedure differed from Method A only in that a solution of 2 g. of sodium hydroxide in 50 ml. of water was added following the sodium acetate solution.

Method C. The procedure differed from Method B only in that 0.05 mole of the amine (as the pure compound) was used rather than a two fold excess, as in Method A and B.

Melting Points. Melting points were determined in open-end capillaries using a Hershberg apparatus and short range Anschütz thermometers (uncalibrated). Values reported in Tables I and II were determined by preheating the bath to 10° C. below the melting point before introducing the capillary. In most cases preheating the bath was unimportant. In the case of bis(N-methylsalicylaldimine) nickel (II), however, the compound decomposed on slow heating to an infusible product before the normal melting point was reached.

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(4) For this purpose it is necessary to insure a small excess of the amine during the preparation of the chelate to prevent the possible coprecipitation of the copper or nickel chelate of salicylaldehyde. A large excess of amine is not harmful for the lower amines but tends to contaminate the product for the higher ones.

The melting points of the chelates studied were found not to change appreciably after storage of the compounds at room temperature for a period of 1 year.

Mixed melting points were determined for the following pairs of compounds after grinding approximately equal quantities together in a small mortar. Values obtained: Copper chelates: methyl-ethyl, 97–100°; heptyl-octyl, 56–61°; decyl-dodecyl, 46–50°; dodecyl-tetradecyl, 45–49°. Nickel chelates: heptyl-octyl, 95–96°; decyl-dodecyl, 72–75°; dodecyl-tetradecyl, 71–74°.

Molecular Weights. The molecular weights of the chelates were determined cryoscopically in 1,4-dioxane using weighed quantities of the solute and solvent and using a thermometer which could be estimated to ±0.01C°. The concentration of the solutions was about 0.1*M*. The apparatus used was capable of an accuracy of about ±5% in the M.W. The dioxane used was refluxed over sodium and distilled through an efficient fractionating column. A value of 4.63 was used for K_f.

Analyses. The organic portions of the compounds were destroyed by repeatedly evaporating with mixtures of hydrochloric, nitric, and sulfuric acids. Copper was determined in the residues gravimetrically with 8-hydroxyquinoline, and nickel gravimetrically with dimethylglyoxime. Nitrogen was determined by the Kjeldahl method using separate samples.

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[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Preparation of *N,N'*-Bis(α-haloacyl)hydrazines[1]

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The preparation of several *N,N'*-bis(α-haloacyl)hydrazines from hydrazine hydrate and α-haloacid halides or α,α'-dihaloacid anhydrides respectively is described.

The well known benzidine rearrangement of hydrazo compounds proceeding under the influence of acids sometimes fails, *e.g.*, with hydrazothiazoles-(2,2').[2] However, in this case, it was found possible to bring about the benzidine rearrangement by means of phthalic anhydride.[3] In order to test the scope of the applicability of the phthalic anhydride reaction on isomeric hydrazothiazoles, an effort was made to synthesize hydrazothiazole-(4,4') and -(5,5'). Interaction of 2,4-dimethyl-5-bromothiazole[4] with hydrazine hydrate in a sealed tube gave only decomposition products. Thiazolinones, such as 2-phenylthiazolinone-(4),[5] do not react with hydrazine hydrate. The *N,N'*-bis(α-haloacyl)hydrazines (II) and thioamides either did not react or formed the ammonium halides as decomposition products. Although synthesis of the hydrazothiazoles-(4,4') or -(5,5') was not achieved, preparation of some α-haloacylhydrazines is described here since examples of this class of substances do not appear to have been recorded previously in the literature.

Although the reaction of acid chlorides (III) with hydrazine hydrate is a standard procedure for preparing *N,N'*-diacyl-hydrazines (IV),[6] no literature references are to be found dealing with the application of this reaction utilizing the simpler acid chlorides, *e.g.* III, R = CH_3, $C_6H_5CH_2$, C_2H_5, or C_3H_7. Consequently, *N,N'*-diphenacetylhydrazine (IV, R = $C_6H_5CH_2$) was prepared from phenacetyl chloride (III, R = $C_6H_5CH_2$) and hydrazine hydrate. These components reacted vigorously to give a 28% yield of IV (R = $C_6H_5CH_2$), a compound hitherto accessible only through protracted procedures.[7]

In a similar manner the preparation of II was accomplished by the reaction of α-haloacid halides (I) with hydrazine hydrate.[8] The investigation of the end products of this reaction indicated the formation of considerable amounts of the corresponding α-haloacids with lesser amounts of II. Better yields of II were obtained by using inert solvents such as

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(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, Baltimore, Md.

(2) D. Markees, M. Kellerhals, and H. Erlenmeyer, *Helv. Chim. Acta*, **30**, 304 (1947); H. Beyer, H. Schulte, and G. Henseke, *Chem. Ber.*, **82**, 143 (1949).

(3) H. Beyer and A. Kreutzberger, *Chem. Ber.*, **84**, 518 (1951).

(4) G. M. Dyson and R. F. Hunter, *J. Indian Chem. Soc.*, **8**, 147 (1931).

(5) P. Chabrier and S. Renard, *Compt. rend.*, **226**, 582 (1948).

(6) H. Wieland, *Die Hydrazine*, Verlag Ferdinand Enke, Stuttgart (1913).

(7) A. Pinner and Göbel, *Ber.*, **30**, 1889 (1897); T. Curtius and E. Boetzelen, *J. prakt. Chem.*, [2] **64**, 318 (1901); G. Klein and W. Fuchs, *Biochem. Z.*, **213**, 49 (1929).

(8) Hydrazine hydrate has been found to effect reductive dehalogenation of some halogenocompounds [see *e.g.* B. W. Howk and S. M. McElvain, *J. Am. Chem. Soc.*, **55**, 3372 (1933)]. Consequently, anhydrous hydrazine was not used by the author since it is known to be an even stronger reducing agent than hydrazine hydrate [see *e.g.*, S. Dutt and K. Sen, *J. Chem. Soc.*, 3420 (1923); 2971 (1925)].