[JOINT CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR & COMPANY AND THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF PURDUE UNIVERSITY]

Complex Formation with High Molecular Weight Amines. I[1]

BY F. K. BROOME, A. W. RALSTON AND M. H. THORNTON[2]

In spite of an extensive literature on the subject of complex compounds comprising amines and metal salts, no reports have listed compounds involving high molecular weight aliphatic amines. In view of the fact that high molecular weight amines possess radically different properties from lower members of the group, it seemed desirable to investigate complex formation between them and the salts of heavy metals. This paper presents a report of the preparation of a number of complexes of high molecular weight amines with metal salts and discusses their composition and properties. It has been limited to the salts of five metals, and to three saturated aliphatic amines, primary and secondary.

Experimental

Starting Materials.—Anhydrous solvents were used throughout. C. P. ether was dried with calcium carbonate and sodium, and ethanol was dried with magnesium turnings and iodine. For the molecular weight determinations, reagent trichloromethane was distilled through a Stedman-packed column, that portion boiling at 61.1° being used.

Dodecylamine and octadecylamine were prepared as previously described[3] and were purified by rectification in a Stedman-packed column. Their freezing points were, respectively: 28.23 and 52.38°. Dioctylamine was prepared as previously described,[4] and was also purified in a Stedman-packed column. By titration with tenth normal acid, its content of dioctylamine was determined to be 97.9%.

Anhydrous cupric acetate was prepared by treating the hydrate with acetic anhydride and distilling off the acetic acid formed. Residual anhydride was removed with anhydrous ether, and the anhydrous salt stored at room temperature in a vacuum desiccator. The salt contained 35.5% copper; theory, 35.0%.

Cupric hydroxide was prepared by the procedure of Hatch,[5] and was then dried at 70°.

Silver chloride was precipitated from a solution of silver nitrate with the theoretical quantity of hydrochloric acid and was dried at 110°. It was protected from the action of light at all times.

All other metal salts were dried simply by heating at 110°.

Methods of Complex Preparation.—Six general methods have been employed in making the complexes described herein. The procedures are summarized below, and reference to them will be made by letter in Table I.

A. One mole of the metal salt dissolved in ethanol was added to an ethanol solution of two moles of the amine with constant agitation at room temperature. The complex usually precipitated out quantitatively at room temperature, but could always be obtained by cooling. It was filtered, washed with ethanol, and dried *in vacuo* at room temperature. Purification was effected by recrystallization from a suitable solvent as indicated.

B. One mole of the metal salt and two to four moles of the amine were covered with a solvent and heated under reflux until reaction was complete. If the reactants, as well as the product, are soluble in the boiling solvent, the reaction is completed almost immediately. The method is sometimes suitable even when the metal salt is not appreciably soluble alone in the solvent, as, for example, in the case of cupric chloride in trichloromethane. The amine evidently increases the solubility of the metal salt. When the solution was cooled, the complex was obtained in crystalline form. Recrystallization was effected from the same solvent, and the product was dried *in vacuo* at room temperature.

C. One mole of the metal salt and two moles of the amine were placed in a flask equipped with a stirrer. The contents of the flask were heated in an atmosphere of nitrogen, stirring being started at the melting point of the amine. Heating was continued until homogeneity was obtained, occasionally at the melting point of the complex, but usually at a considerably higher temperature. Temperatures as high as 170° have been required. After cooling, the solidified cake was covered with solvent, dissolved by heating, and recrystallized as above. Although less desirable than the others, this method occasionally was the only method which would serve.

D. The metal hydroxide and the alkylammonium chloride were mixed in the molar ratio of 1:2 in trichloromethane, and heated to boiling. The complex chloride was formed with the splitting out of water, and recrystallization and drying were effected as before.

E. The double salt (v. i.) formed from two moles of alkylammonium halide and one mole of metal halide was treated, in water or alcohol solution, with the theoretical amount of aqueous sodium hydroxide, precipitating the complex and forming sodium halide.

F. The above-mentioned double salt, dissolved in ethanol, was treated with an excess of amine in alcoholic solution, precipitating the complex and leaving alkylammonium halide in solution. In the last two methods, as before, the complex was recrystallized, and dried *in vacuo*.

Complex Compounds Prepared.—In Table I are listed the compounds prepared, together with their analyses and some of their physical properties.

The compounds listed are all insoluble in cold water. They are decomposed by boiling water, yielding free amine, metallic oxide or hydroxide, and probably amine hydrochloride and basic metal salt. Thus it has been found possible to recover roughly half the amine by steam distillation from a mixture of water and bisdodecylammino-cupric chloride. In general, the chlorides are soluble in hot trichloromethane, and relatively insoluble in it at room temperature. An exception is the secondary-amine complex, which is very soluble in cold trichloromethane. The chloride complexes which contain primary amine are somewhat soluble in hot ethanol, while the secondary amine complex is decomposed by this solvent. The latter compound is very soluble in hot ether, petroleum ether and isobutanol. The acetates are very soluble in trichloromethane and in hot ethanol, with a somewhat lower solubility in hot ether. The silver nitrate complex is readily soluble in hot ethanol, while the zinc bromide complex dissolves with ease in hot ethanol, ether and petroleum ether.

A complex compound, formed from dodecylamine and silver chloride, has been prepared in very impure form. The best preparation was obtained by method C, at a temperature somewhat above 150°. No solvent could be found for recrystallization, but it was washed as thoroughly as possible with benzene. The washed material melts sharply at 71.5°, without decomposition in the dark, but

---

[1] Journal Paper No. 230 Purdue University Agricultural Experiment Station.

[2] M. H. Thornton is a member of the Department of Agricultural Chemistry, Purdue University Agricultural Experiment Station, Lafayette, Indiana.

[3] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, 63, 1598 (1941).

[4] Hoerr, Harwood and Ralston, *J. Org. Chem.*, 9, 201 (1944).

[5] Hatch, *Ind. Eng. Chem.*, *Anal. Ed.*, 16, 104 (1944).

TABLE I

A = Dodecylamine, $C_{12}H_{25}NH_2$; A′ = octadecylamine, $C_{18}H_{37}NH_2$; A″ = dioctylamine, $(C_8H_{17})_2NH$

Formulas	Meth. of prepn.	Solv.	Form	M. p., °C.	Composition, % Metal		Amine		Anion	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
CuA_2Cl_2[a]	A, B, C, D, E, F	$CHCl_3$	bl. fl.	128	12.5	12.5	73.4	73.1	14.0	14.0
$CuA_2(OAc)_2$[b]	B	C_2H_5OH	Purp. pr.	86	11.5	11.7	67.1	67.0	..	..
AgA_2NO_3	A, B	C_2H_5OH	Wh. fl.	75 d.	20.0	21.4[c]	68.5	66.3[c]	11.5	11.1[c]
ZnA_2Cl_2	A, B	$CHCl_3$	Sm. wh. fl.	135–136	12.9	12.9	73.1	72.7	14.0	14.1
ZnA_2Br_2	A	Ether, pet. ether	Wh. cr.	137–140	..	..	62.3	62.2	26.8	26.9
CdA_2Cl_2	A, B	$CHCl_3$	Glit. wh. cr.	141–142	21.3	21.5	66.9	66.9	12.8	12.9
HgA_2Cl_2	A, B	$CHCl_3$	Sm. glit. wh. cr.	155–156 d.	31.2	31.2	57.8	57.6	11.0	11.1
CuA'_2Cl_2	A	$CHCl_3$	Bl. fl.	126	9.5	9.2	80.0	79.5	10.5	10.0
$CuA'_2(OAc)_2$	B	C_2H_5OH	Purp. cr.	95.5–96	8.8	8.4	74.8	74.0	16.4	17.4
CuA''_2Cl_2	B	Ether	Dark bl. cr.	126–127	10.3	10.4	78.2	78.1	11.5	11.7

[a] Mol. wt.: calcd. 505; found, 603. [b] Mol. wt.: calcd. 552; found, 578. [c] Because of its photosensitivity, this compound has not been obtained free from impurities.

without becoming entirely clear. It is photosensitive, darkening rapidly in a bright light. An analysis of the product obtained showed 37.6% silver, 48.6% amine and 12.7% chlorine. This corresponds to a structure involving three amine groups to four of silver chloride. It is believed the analysis merely shows the presence of silver chloride as a contaminant in the usual 1:2 complex. The product, white when protected from light, is insoluble in water, ether, trichloromethane, benzene, and acetone, and decomposes in methanol, apparently to silver chloride and amine, the latter going into solution.

In addition to the complex compounds, two double salts were prepared during the course of this study. They are cupric dodecylammonium chloride and cupric octadecylammonium chloride. In composition, modes of preparation, color and physical properties the two resemble each other very closely. Thus it will suffice to describe only the former in detail.

If an excess of cupric chloride in ethanol solution is added to an alcoholic solution of dodecylamine, the blue complex bisdodecylamminocupric chloride is not formed. Rather there precipitates from the solution a yellow product with a Cu:A:Cl ratio (where A represents amine) of 1:2:4, which proves on complete investigation to be the double salt $CuCl_2 \cdot 2AHCl$. This salt can be prepared in a variety of ways. The two components, cupric chloride and dodecylammonium chloride, may be mixed in the correct proportion in water or alcohol solution, forming the compound in solution (in water, it exists as its ions). It may be formed from bisdodecylamminocupric chloride by treatment in alcohol suspension or trichloromethane solution with hydrochloric acid, or by treatment with chlorine gas (which contains or can form hydrogen chloride). It has also been formed from bisdodecylamminocupric acetate with an excess of hydrochloric acid.

This double salt crystallizes from ethanol in beautiful yellow flakes which have no melting point up to 200°, but which change reversibly to a golden color at about 100°, the normal color returning on cooling. It is soluble (with ionization) in water, soluble in alcohol, and insoluble in trichloromethane.

Anal. Calcd.: Cu, 11.0; Amine, 64.2; Cl, 24.6. Found: Cu, 10.9; Amine, 64.3; Cl, 24.7.

Its 0.01 *m* aqueous solution has a conductivity of 189 mhos. at 25°. That calculated from the values for cupric chloride and dodecylammonium chloride is 200.5 mhos. The lower value obtained may be ascribed to the common ion effect.

Analytical Procedures.—Standard procedures as outlined by Scott[6] were used for the analyses of metals and anions. The method of Ralston and Hoerr[7] for amine was applied in the case of the dodecylamine-copper and -zinc derivatives simply by placing a sample of complex in a Kjeldahl flask with dilute sodium hydroxide solution, and distilling into standard acid. Hot alkaline solutions invariably destroy the complexes. In the presence of silver or mercury, however, it was necessary to add sodium sulfide to the alkaline solution before distilling, else the amine results were low. The octadecylamine and dioctylamine analyses were conducted by the Kjeldahl procedure, using cupric sulfate as catalyst, while the cadmium complex was analyzed by the Kjeldahl-mercuric oxide method. For the molecular weight determinations, the apparatus and method of Menzies[8] were employed, using trichloromethane as the solvent. It is not surprising that the molecular weights determined by this method on such large molecules are not in very good agreement with the theoretical values, inasmuch as the vapor-pressure lowering was in the neighborhood of three to four millimeters at the concentration which could be employed.

The conductivity measurements on the double salts were performed at 25° in a cell having a constant, *K*, of 0.585.

Discussion

Preparations.—The methods of preparation necessarily differ from those in use for the preparation of complex compounds containing low molecular weight amines. Most metal salts are insoluble in the majority of organic solvents, while on the other hand the high molecular weight amines are in all cases immiscible with water. These amines are unable to displace water from metal–salt hydrates, and the salts employed must be dried before use. Consequently, anhydrous solvents are needed. If water is present, the usual product of the reaction between an amine and a metal salt appears to be a basic salt of the metal. It is to be noted that method E involves the use of water. In this case, however, the presence of the double salts hinders the formation of a hydrate, and the amine is enabled to react.

In the case of low molecular weight amines, the reactants can be brought together easily, since the amine can be obtained in the vapor state. In the present work, however, it is advantageous to have recourse to a solvent. Preparations made by method C, in which amine and metal salt are heated without solvent, resemble those involving low molecular weight amines,

---

[6] "Scott's Standard Methods of Chemical Analysis," Furman, editor, 5th ed., D. Van Nostrand Company, Inc., New York, N. Y., 1939.

[7] Ralston and Hoerr, *Ind. Eng. Chem., Anal. Ed.*, **16**, 459 (1944).

[8] Menzies, THIS JOURNAL, **32**, 1615 (1910).

except that the reactants must be strongly heated. A considerable loss of the amine at elevated temperatures decreases the yields obtainable. Ethanol is a good solvent for many of the reactions since many heavy metal salts, notably the chlorides, are soluble in it. However, in those cases where the amine in trichloromethane solution renders the salt sufficiently soluble, the added advantage of solubility of the product exists.

Amine–Metal Ratio.—Every complex compound prepared between high molecular weight amines and metal salts contains the ratio of amine to metal of 2:1. The rule may not be universally applicable, but all attempts made to prepare compounds containing more amine have met with failure. It has been possible with copper salts to obtain substances which are a deeper blue than the 2:1 complexes, but these are not pure. They contain no simple ratio of amine to metal and they cannot be recrystallized without decomposition. Perhaps the attraction of the high molecular weight amine molecule for the metal is not strong enough to displace the anions from the coördination sphere. Some evidence of this behavior is to be found in the literature, where it is reported that compounds between amines and a metal contain less amine the higher the weight of the amines. For example Straumanis and Cirulis[9] found that a greater ratio of amine to metal can be obtained with methylamine than with higher amines, in combination with mercury and copper halides. Fricke and Röbke[10] reported that a 1:4 complex of beryllium chloride and *n*-butylamine tended to decompose on washing with ether, while a 1:2 complex was stable. The size of the amine molecules may have something to do with their inability to occupy the maximum number of coordination spots around a central atom.

The ratio of amine to metal in the double salts of alkylammonium chlorides with copper chloride is also 2:1, but a different reason must be assigned for this fact. The yellow-brown color of anhydrous cupric chloride, the yellow color of its concentrated alcoholic solution, and the yellow color of its hydrochloric acid solution have been ascribed[11] to the presence of the complex ion $[CuCl_4]^{2-}$. By analogy, the yellow alkylammonium double salts may be considered to contain this grouping. They may thus be represented by the formula $[CuCl_4](AH)_2$, where A represents amine. Thus the ratio of 2:1 is necessitated by the 4-coördination power of the copper atom. No explanation is advanced for the color shift from yellow to gold when the double salts are heated.

Summary

1. The preparation and properties of the following complex compounds have been described: bisdodecylammino-cupric chloride, bisdodecylammino-cupric acetate, bisdodecylammino-silver nitrate, bisdodecylammino-zinc chloride, bisdodecylammino-zinc bromide, bisdodecylammino-cadmium chloride, bisdodecylammino-mercuric chloride, a dodecylamine-silver chloride complex, bisoctadecylammino-cupric chloride, bisoctadecylammino-cupric acetate and bisdioctylammino-cupric chloride.

2. Pure compounds containing more than two amine groups in the molecule have not been obtained, perhaps because the high molecular weight amines do not possess sufficient attractive force for the central metallic atom to drive the anionic residues from the coördination sphere.

3. The preparation and properties of two double salts, cupric dodecylammonium chloride and cupric octadecylammonium chloride, have been described.

4. Because of their color the double salts are believed to contain the grouping $[CuCl_4]^{2-}$, and the correct formula for these compounds is thus $[CuCl_4](AH)_2$, where AH represents the alkylammonium radical.

CHICAGO, ILLINOIS RECEIVED AUGUST 13, 1945

---

[9] Straumanis and Cirulis, *Z. anorg. allgem. Chem.*, **230**, 65 (1936); **234**, 17 (1937).

[10] Fricke and Röbke, *ibid.*, **170**, 25 (1928).

[11] Moeller, *J. Phys. Chem.*, **48**, 111 (1944).