High Molecular Weight Aliphatic Amine-Metallic Complexes*

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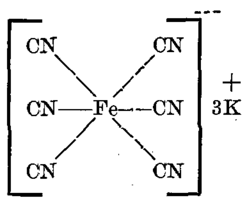
THE theory of Werner in which it is postulated that elements possess two kinds of valence, termed principal and auxiliary valencies, is well known to chemists. A compound such as potassium ferricyanide when dissolved in water yields potassium and ferricyanide ions and may be represented by the following structural formula:



The ammino complexes are among the most common of the coordination compounds and present outstanding illustrations of this type of compound. Those formed between copper salts and ammonia are probably the most familiar of the ammino complexes. The deep-blue solution which results upon the addition of ammonium hydroxide to a solution of copper sulfate is due to the formation of a complex of the formula $CuSO_4 \cdot 4NH_3 \cdot H_2O$. Other cuprammino sulfates are known to exist, such as pentammino-cupric sulfate, $[Cu(NH_3)_5]SO_4$, and diammino-cupric sulfate, $[Cu(NH_3)_2]SO_4$. Cuprammines have been obtained from many other copper salts.

It has been known that the lower molecular weight amines, such as methylamine, are capable of forming coordination compounds with heavy metal salts (1). Such compounds probably possess structures similar to the ammines. Until comparatively recently no one has shown it to be possible to prepare metallic complexes involving metallic salts and the higher molecular weight amines. The preparation of such compounds is attended by difficulties not encountered with ammonia or the low molecular weight amines. Complexes between metallic salts and ammonia or low molecular weight amines are easily prepared by treating the salt with gaseous ammonia or amine, or by adding an aqueous solution of ammonium hydroxide or amine to an aqueous solution or suspension of the metallic salt. Such procedures would be precluded with the higher alkylamines because of the high boiling point and water insolubility of such amines. This necessitates that entirely different methods be employed for their preparation. Quite recently, Broome, Ralston, and Thornton (2) have described the preparation of a number of high molecular weight amine-metallic complexes and have studied the general properties of such compounds. Six alternate procedures were developed for the synthesis of these complexes, the particular method employed depending upon the compound in question. These procedures are as follows: (1) An ethanol solution of one mole of the metal salt is added to two moles of the amine dissolved in ethanol. The mixture is cooled and the precipitate washed with ethanol. (2) A mixture of the amine and the metal salt is refluxed with an organic solvent. (3) A mixture of the amine and the metal salt is heated in an inert atmosphere with stirring. (4) The metal hydroxide and an alkylammonium chloride in the molecular ratio of 1:2 are refluxed in chloroform. (5) A double salt of a heavy metal and an amine is treated with the theoretical amount of sodium hydroxide in aqueous or ethanol solution, thus precipitating the metallic complex. (6) The double salt of an amine and a heavy metal is treated with an excess of the amine in ethanol solution. Table 1 shows the physical properties of several high molecular weight amine-metallic complexes.

TABLE 1.
$A = C_{12}H_{25}NH_2$; $A' = C_{16}H_{33}NH_2$; $A'' = C_{18}H_{37}NH_2$; $A''' = (C_8H_{17})_2NH$.

Formula	Method	Solv.	Form	M.P.°C.
CuA_2Cl_2	1,2,3,4,5,6	$CHCl_3$	Blue flakes	128
$CuA_2(OAc)_2$	2	C_2H_5OH	Purple prisms	86
$CuA_2(C_{18}H_{37}CO_2)_2$	2	C_2H_5OH	Blue crystals	77-79
AgA_2NO_3	1,2	C_2H_5OH	White flakes	75 (decomp.)
ZnA_2Cl_2	1,2	$CHCl_3$	Small white flakes	135-136
ZnA_2Br_2	1	Ether Petr. ether	White crystals	137-140
CdA_2Cl_2	1,2	$CHCl_3$	Glittering white crystals	141-142
HgA_2Cl_2	1,2	$CHCl_3$	Small glittering white crystals	155-156
CoA'_2Cl_2	1	C_2H_5OH	Deep-blue crystals	....
$CuA_2''Cl_2$	1	$CHCl_3$	Blue flakes	126
$CuA_2''(OAc)_2$	2	C_2H_5OH	Purple crystals	95.5-96
$NiA_2''(HCO_2)_2$	2	$CHCl_3$	Blue, amorphous	....
$CuA_2'''Cl_2$	2	Ether	Dark-blue crystals	126-127

The high molecular weight amine-metallic complexes are insoluble in water. They are, in general, soluble in organic solvents, the solubility depending upon the specific complex in question. It will be noted that all the complexes shown in Table 1 have an amine-metal ratio of 2:1. All attempts to prepare complexes having a higher amine to metal ratio have so far been unsuccessful. A spectrophotometric study of the system dodecylamine-cupric acetate (3) presented no evidence for the existence of complexes containing a higher ratio of amine to metal than 2:1.

The complexes formed between the higher alkylamines and metallic salts are an interesting group of compounds. Their potential importance resides in the fact that they constitute a series of organic com-

* Presented by A. W. Ralston before the American Oil Chemists' Society, Edgewater Beach Hotel, Chicago, Illinois, Oct. 29-Nov. 1, 1946.

pounds containing high percentages of heavy metals. In this respect they are comparable to the heavy metal soaps which have been important industrial chemicals for many years. It is quite possible that a number of the functions now performed by the heavy metal soaps can be better accomplished by the use of these complexes.

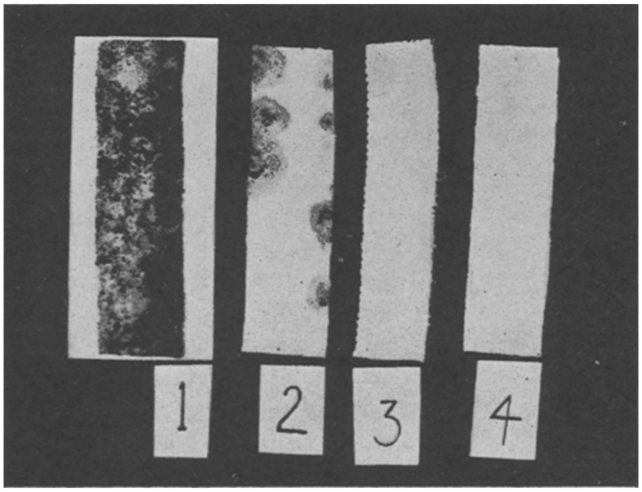


FIG. 1. Canvas strips inoculated with *Chaetomium globosum*.
1. Untreated.
2. 1.5% Bishexadecylammino-zinc chloride applied in carbon tetrachloride solution.
3. 1.5% applied as emulsion.
4. Bishexadecylammino-mercuric chloride.

Several uses for these complexes have already been investigated, and among these may be mentioned their application as insecticides and fungicides. It is known that the higher alkylamines themselves are quite lethal to the lower forms of both animal and plant life. Complexes between such amines and the salts of metals such as copper and zinc should, therefore, be quite effective fungicides since these metals also exhibit high fungicidal properties.

One of the most interesting uses for fungicidal agents is in the treatment of fabrics and allied materials for protection against molds and rot-producing organisms. Fig. 1 shows several pieces of cotton duck which have been inoculated with the mold *Chaetomium globosum* and held for fourteen days under conditions favorable to mold growth. Sample 1 is the untreated cloth. The second sample contains approximately 1.5% of bishexadecylammino-zinc chloride, which was applied by dipping the cloth in a carbon tetrachloride solution of the complex. The third sample also contains approximately 1.5% of

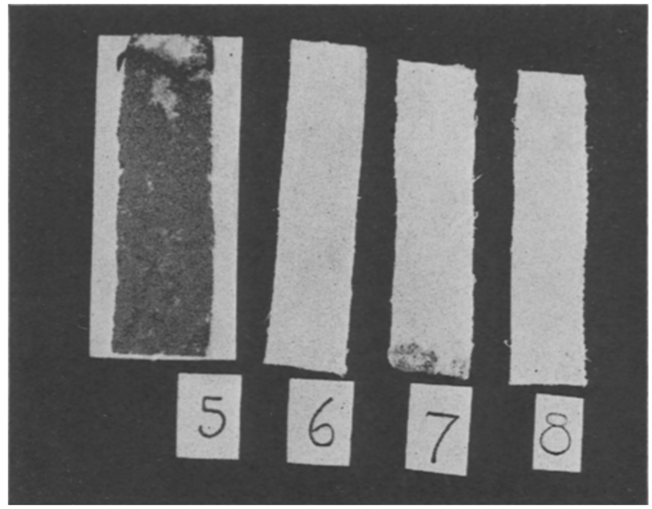


FIG. 2. Canvas strips inoculated with mold of *Metarrhizium* species.
1. Untreated.
2. 1.5% Bishexadecylammino-zinc chloride applied in carbon tetrachloride solution.
3. 1.5% applied as emulsion.
4. Bishexadecylammino-mercuric chloride.

this amine complex, applied as an emulsion, and the fourth sample contains bishexadecylammino-mercuric chloride applied through a carbon tetrachloride solution of the complex. The inhibition of mold growth, especially in samples 3 and 4, is quite apparent. Tests now underway indicate that the treated cloths retain a substantial portion of their resistance to mold growth after washing.

A similar series of tests in which a mold of the *Metarrhizium* species was employed is shown in Fig. 2. The protective action of the amine-metallic complexes is again clearly evident. The copper-amine complexes have been shown to be as effective as those of zinc or mercury. However, the fact that the copper-amine complexes are highly colored would greatly reduce their commercial interest as textile treating agents.

Textile treatment is only one of the many uses which can be suggested for the high molecular weight amine-metallic complexes. Considerable time will probably elapse before many of these uses are properly evaluated.

REFERENCES

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