



Synthesis and structural study of some new alkylammonium tetrachlorometallates (11)  
by Uma Prasad Tripathi

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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Abstract:

Tetrachloro alkylammonium salts of zinc, manganese, and copper were prepared. The structure of  
n-propylammonium tetrachlorozincate(II) was determined.

The powder diffraction and refractive indices data were obtained on almost all of the compounds and  
structural correlations were made.

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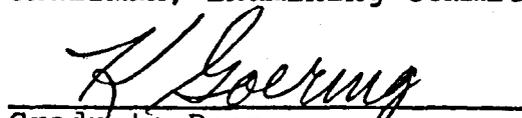
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Chemistry

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## ABSTRACT

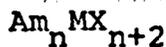
Tetrachloro alkylammonium salts of zinc, manganese, and copper were prepared. The structure of n-propylammonium tetrachlorozincate(II) was determined. The powder diffraction and refractive indices data were obtained on almost all of the compounds and structural correlations were made.

## INTRODUCTION

### History

The crystals of transition metal co-ordination compounds are frequently not built of the same structural units as occur in solutions, metals, or vapors. This has inspired many chemists and physicists to study the solid state. In order to elucidate the atomic and electronic structures of solids, magnetic, X-ray diffraction and spectroscopic studies are most frequently used. The study of the spectra of atoms and molecules can lead to a detailed insight into their structures. The spectral data help to determine not only the symmetry of ligands around metal atoms in a molecule but also the strength of the forces which bind them together and the relationship between these forces and the possible arrangement of the electrons in atoms and molecules. The gross structure of any solid can only be determined by X-ray diffraction studies. Recently, computer time has become relatively less expensive and there are now computer controlled diffractometers on the market. A complete structure analysis, however, is still very time consuming and costly.

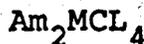
Alkylammonium halogenometallates are one set of compounds whose structural pattern in solids and solutions are not the same. Remy and Laves<sup>1</sup> were the first workers to prepare a large number of these alkylammonium salts using alkyl-amine hydrochlorides and copper(II) chlorides. Since the late 1950's many more compounds of this nature have been prepared. These compounds may be represented by the following general formula:



Where X is a halogen and n is an integer between 1 and 4.

Here we will consider only those cases where n=2 and x=Cl.

This class of compounds may be represented by the following formula:



Where: Am = any ammonium, alkylammonium or quaternary ammonium.

M = any divalent transition metal ion of first row such as Fe, Co, Ni, Cu, and Zn.

Copper salts. Most of the early work was concentrated on tetrachlorocuprates. In general, these compounds were isolated by evaporating the ethanol solution containing stoichiometric amounts of metal(II) chloride and amine

hydrochloride. In most cases, the salts crystallize in the form of thin yellow sheets or green needles.

These particular compounds exhibit two geometric arrangements of the chlorine about a central copper atom. The first one is a modified type of perovskite structure in which layers of  $\text{CuCl}_4^-$  ions (square-planar) group together and share corners to give a distorted octahedral<sup>3</sup> co-ordination about the metal ion. These  $\text{CuCl}_4^-$  layers are separated by layers of alkylammonium cations. The  $\text{CuCl}_4^-$  layer is illustrated in Figure 1.

The other observed co-ordination is a distorted tetrahedral structure in which the four chlorines are arranged about the copper at the corners of a flattened tetrahedron. The flattening of the  $\text{CuCl}_4^-$  tetrahedron has been rationalized on the basis of the crystal field theory<sup>5</sup> together with the theory of Jahn and Teller<sup>6,7</sup>. In a perfect octahedral environment, the ground state  $E_g$  of Cu(II) has an electronic hole which is twofold degenerate. The Jahn Teller theorem asserts that for such an orbitally degenerate case there will always be some non-totally symmetric displacement of the nuclei towards which the totally symmetrical configuration will be unstable and so the molecule

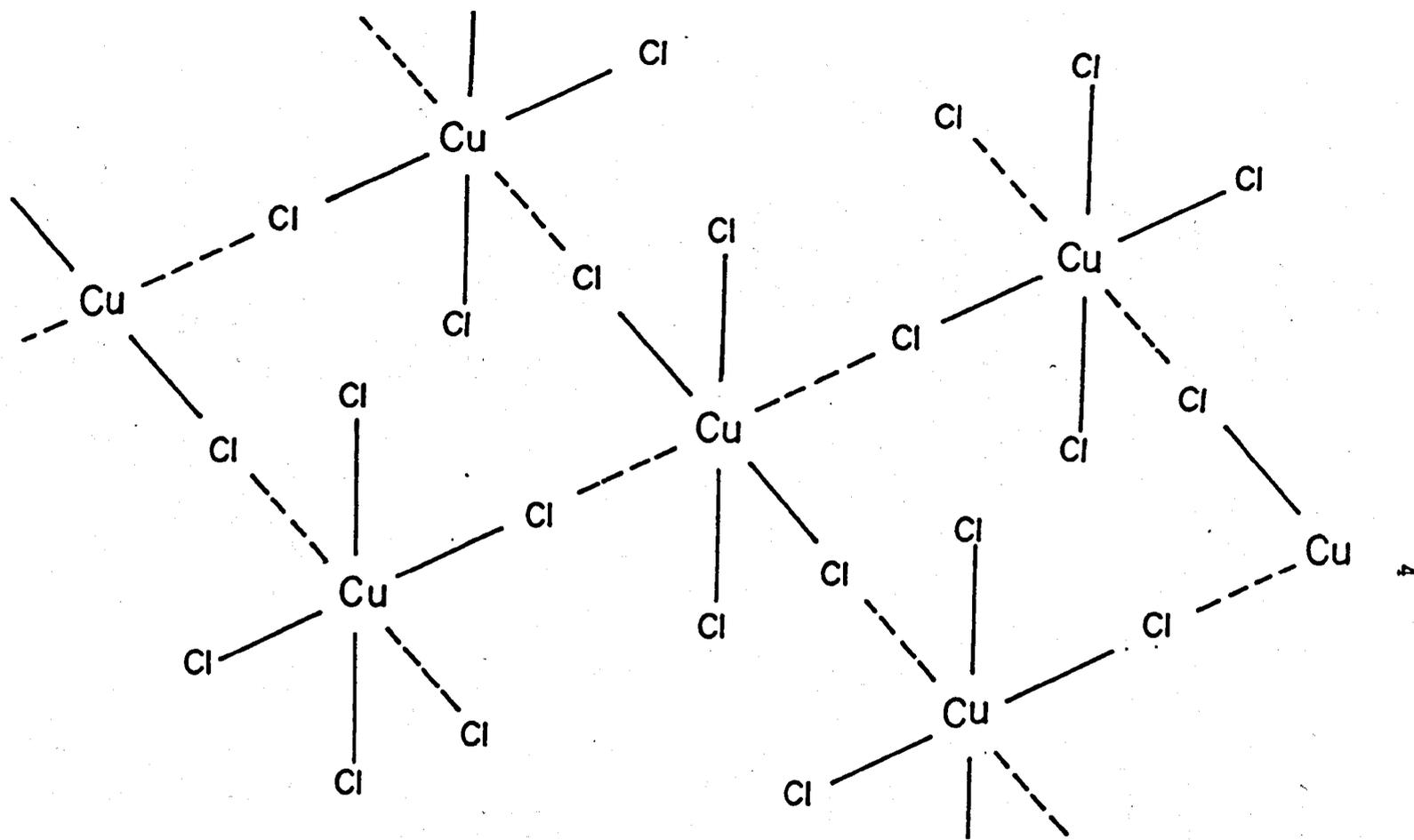


Figure 1. Copper Complex with  $O_h$  Symmetry

will distort into a new shape. Figure 2 shows the vibrations which are capable of distorting the perfect octahedral nuclear configuration when the molecule possesses an orbital degeneracy. The four possible distorted shapes are also illustrated.

In Figure 2a, the distortion is such that two of the transmetal-ligand distances are greater than the other four. This type of distortion is known for several  $\text{CuCl}_4^-$  ions. In a few cases such as  $\text{K}_2\text{CuF}_4$ , four longer distances and two shorter distances are observed. This is illustrated in Figure 2b. No structures of the type 2c and 2d are yet known.

It is known the  $\text{CuCl}_4^-$  ions, as they occur in their cesium salt, are tetrahedral though the tetrahedrons are decidedly flattened<sup>8</sup> as shown in Figure 3. In a regular tetrahedron, all four angles will be  $109^\circ$ , but when the tetrahedron is flattened, two of the angles will be larger than the other two. If the larger angles are represented by  $\alpha$  and the smaller by  $\beta$ , the flattening of the tetrahedron could be illustrated as shown in Figure .

In the study of two tetrahedral copper complexes, it has been reported by Lingafelter<sup>38</sup> and co-workers, as

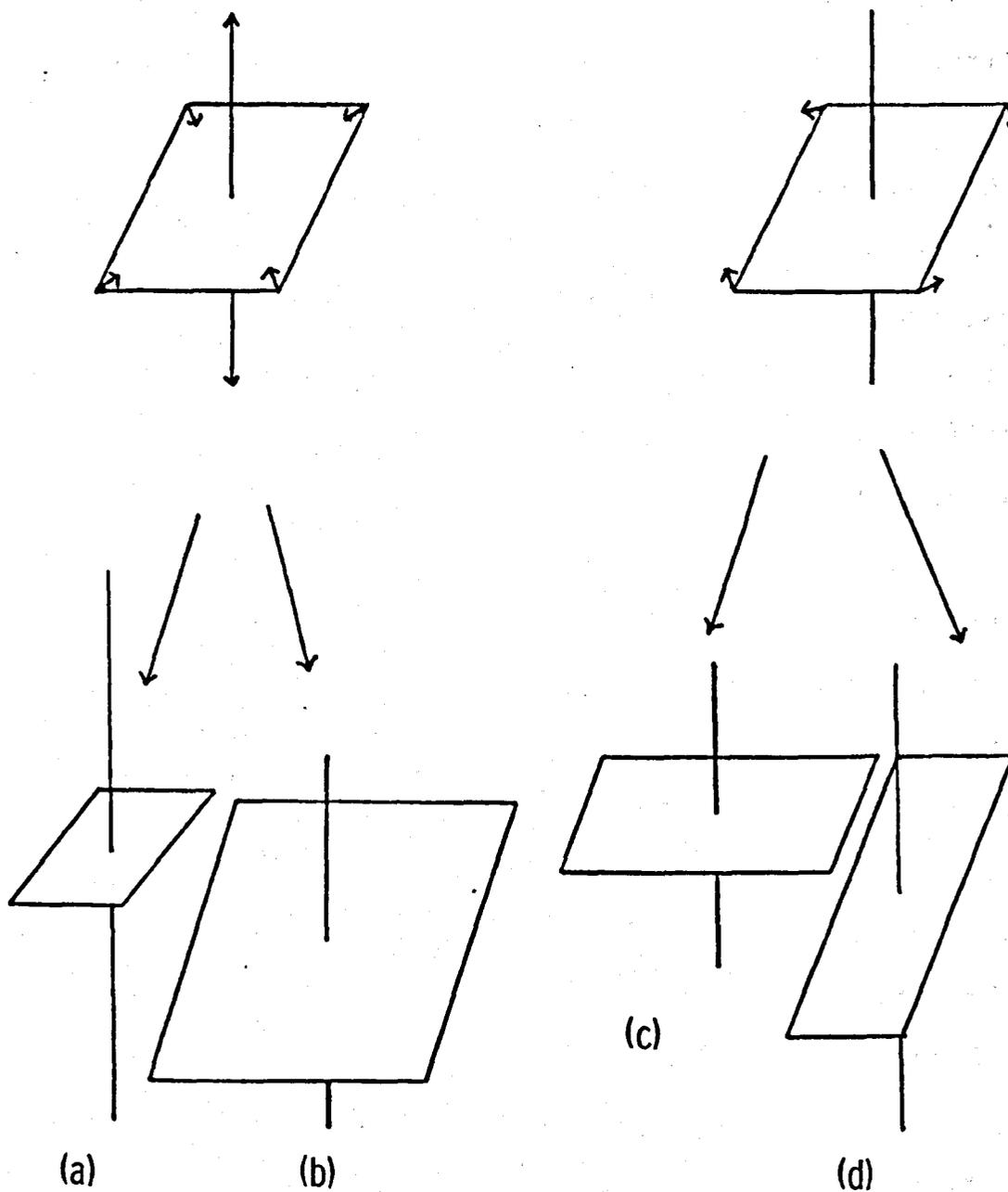


Figure 2. Jahn-Teller Distortion in Octahedral Complexes

well as by Helmholtz and Kruh<sup>9</sup>, that two of the tetrahedral angles are larger than  $109^\circ$  and the other two are smaller than  $109^\circ$ .

The spectrum of tetrachlorocuprates has been discussed by several authors<sup>10-14</sup>. Furlani and Morpurgo<sup>10</sup> suggested that the yellow coloration of the species present is due to a tetrahedral  $\text{CuCl}_4^-$  ion which is<sup>14</sup> present in the orange compound  $\text{Cs}_2\text{CuCl}_4$ . However, according to Willett and Ferguson<sup>11</sup>, the color has been attributed to some kind of charge transfer mechanism operating from the halide ions to the copper ions. Both the square planar and the tetrahedral species showed a large number of intense bands in the visible and ultra-violet regions and a broad unsymmetric band of medium intensity in the near infra-red regions. The absorptions in the visible and ultra-violet have been assigned as charge transfer bands, whereas the absorption in infra-red is believed to be d-d bands of the central ion. Generally, similar spectra are observed in solution, but there are differences in detail.

In a tetragonal species one would expect three d-d transitions, however, only one broad band is reported<sup>14</sup> with the maximum around  $12,800 \text{ cm}^{-1}$ . There is also a shoulder near  $10,500 \text{ cm}^{-1}$ . The extinction coefficient for

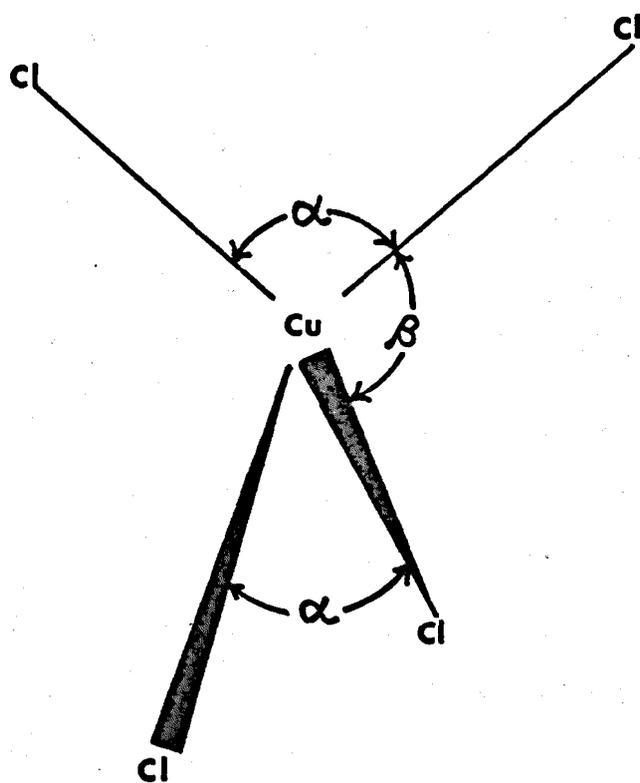


Figure 3. Distorted Tetrahedral Structures of  $(\text{CuCl}_4)^{2-}$  Ions

$$\alpha > \beta$$

this band is reported to be smaller than those of tetrahedral species.<sup>10</sup> All these extinction coefficients were measured in the solution. These extinction coefficients are also highly sensitive to the trace quantities of water present in the solvents. Tables I and II show some of the assignments made for d-d bands in tetrahedral and octahedral complexes.

In the compounds when the chlorines assume a more or less tetrahedral geometry, the observed frequency for d-d transition bands is between 6-9000  $\text{cm}^{-1}$ . Further, the d-d bands are broad and seem to contain more than one transition. Under symmetry  $T_d$  only one transition namely from  $2T_2$  to  $2E$  of  $(3d^9)$  ( $T_d$ ) of copper is expected. On the basis of a strongly distorted tetrahedral model, calculations were done by Ferguson<sup>11</sup> showing four d-d transitions. He also suggested that possibly all four transitions are observed under a broad band at 6000 to 9000  $\text{cm}^{-1}$ .

As assigned by Ferguson<sup>11</sup>, the transitions for charge transfer bands are primarily from ligand orbitals to the highest antibonding d orbitals. The transition energies for the nonbonding orbitals to the antibonding d orbitals are lower compared to those for the bonding orbitals to the antibonding d orbitals. The position of these

Table I  
Spectra of the Tetrahedral  $\text{CuCl}_4^-$  Species

d-d transition	$\text{Cs}_2\text{CuCl}_4^a$ $\text{cm}^{-1}$	$(\text{CH}_3)_4\text{N})_2\text{CuCl}_4^b$ $\text{cm}^{-1}$
$dz^2 \rightarrow dxy$	9000	9000
$dx^2 - y^2 \rightarrow dxy$	7900	
$dxz \rightarrow dxy$	5500	6000
$dyz \rightarrow dxy$	4800	

Table II  
Spectra of the Squareplanar  $\text{CuCl}_4^-$  Species

d-d transition	$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4^b$ $\text{cm}^{-1}$	$(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4^b$ $\text{cm}^{-1}$
$dxz, dyz \rightarrow dx^2 - y^2$		
$dxy \rightarrow dx^2 - y^2$	13,000	12,800
$dz^2 \rightarrow dx^2 - y^2$	10,700	10,500

a - reference 11

b - reference 14

bands was shown by Willett and co-workers<sup>14</sup> to be relatively insensitive to actual co-ordination geometry as long as there was no drastic change in the nature of the bonding. Indeed, there is a small shift in their positions going from octahedral to tetrahedral species but not nearly as large as observed for the d-d transition bands. In general, the positions of the charge transfer bands are the same in both octahedral and tetrahedral cases, whereas the positions of d-d bands are the distinguishing features between these compounds.

Several of the complexes exhibit thermochromism in the solid state<sup>20-23 and 26</sup>. Most of the monoalkylammonium tetrachlorocuprates exhibit a high temperature yellow form and a low temperature green form. The transition temperature is sometimes sharp and varies from compound to compound anywhere between 60 degrees °C. to -78 degrees °C. Usually the color change is very distinct from yellow to light green.<sup>23</sup>

A structural investigation of the low temperature phase of  $\text{Cu}((\text{CH}_3)_2\text{CHNH}_3)_2\text{Cl}_4$  shows that two-thirds of  $\text{CuCl}_4^-$  ions are rearranged in such a way that Cu atoms on the edges assume a square pyramidal configuration. The other one-third of the copper atoms remain unchanged in

the octahedral environment. The spectra of  $\text{Cu}(\text{CH}_3\text{NH}_3)_2\text{Cl}_4$ ,  $\text{Cu}(\text{C}_2\text{H}_5\text{NH}_3)_2\text{Cl}_4$  and  $\text{Cu}((\text{CH}_3)_2\text{CHNH}_3)_2\text{Cl}_4$  in their low temperature form is reported.<sup>14</sup> Because of the similarity between their spectra, it is assumed that the low temperature thermochromic forms of the above three compounds have the same structure. The phase transition in these compounds is believed to be related to the N-H-Cl hydrogen bonding network. It is also possible that the transition reflects order or disorder phenomena. Further spectral and resonance studies of several other compounds in the low temperature phase are needed to provide a better understanding of the thermochromism in these compounds.

Manganese salts. The structural pattern of alkylammonium tetrachlorocuprate salts is at least partly repeated by divalent manganese salts. A detailed investigation of some of the manganese salts has recently been reported by Foster and Gill<sup>24,25</sup> of the Australian National University. They prepared several compounds containing manganese(II) in an octahedral environment. Similar tetrahedral salts of manganese(II) have been extensively studied by several people, including Gill and co-workers<sup>27-30</sup>. In manganese salts it is very easy to distinguish visually

between the tetrahedral and octahedral complexes; most of the known octahedral complexes of Mn(II) are pink in color, whereas the tetrahedral complexes are generally green.

Gill was interested in the analysis of their electronic spectra and the calculations of spectroscopic parameters. Since manganese(II) has a high spin  $d^5$  electronic configuration, the same type of energy diagram applies, whether the environment of metal ions is octahedral or tetrahedral. The only difference is that the energy difference between the similar transitions are different for tetrahedral and octahedral geometrics and also the order of transitions are changed. The ground state of the metal ions with high spin arrangements of the electrons is the  $6A_1$  state and six absorption bands in the visible and near the ultra-violet region of the spectrum corresponds to the spin forbidden transitions from this state to the levels arising from the 4G, 4P, and 4D excited states of the free ion. A further three absorption bands due to transitions to the levels arising from the 4F state occur in the ultra-violet region. The spectra of compounds containing tetrahedral chloro complexes are essentially the same irrespective of the alkylammonium cations present. These band position are given by Cotton.<sup>27</sup>

The crystallographic study of the compounds of the type  $\text{Am}_2\text{MnX}_4$  is also very incomplete; only two monoalkylammonium salts have been studied so far. Willett<sup>49</sup> recently reported the structure of n-propylammonium tetrachloromanganate(II) where manganese is surrounded by six chlorines in an octahedral environment. The powder pattern of  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  has been indexed<sup>25</sup> in terms of both a tetragonal and a hexagonal unit cell. No evidence of thermochromism has been reported in any of the manganese salts studied to date.

Other Divalent Transition Metal Salts

Gill<sup>25</sup> has also investigated some bis tetraalkylammonium tetrachloroferrates and concluded on the basis of the spectral data and magnetic data that these all contain tetrahedrally co-ordinated iron.

Quite a number of workers have examined the spectra and magnetic properties of ammonium and alkylammonium tetrachlorocobaltates<sup>32-36</sup>. The data in all cases have been explained using a tetrahedral model, but the only crystal structures which have been investigated are the cesium salt<sup>37</sup>, the tetramethylammonium salt<sup>38</sup>, and the triphenylmethylarsonium salt<sup>28</sup>. A comparison of the spectra of the tetrahedral  $\text{CoCl}_4^-$  units in the solid phase<sup>32</sup> and octahedral  $\text{CoCl}_6^{4-}$  units<sup>33</sup> indicates that a distinction between these two configurations on the basis of spectra alone is very difficult to make. The magnetic susceptibility has also been used as a criterion to distinguish these configurations, but in, at least some cases, even this data is equivocal for tetrachlorocobaltates.<sup>40</sup>

Tetrachloronickelates have proved to be very difficult to prepare; the only compound reliably reported in the solid state is the tetramethylammonium salt<sup>38</sup>, which has the expected tetrahedral structure.

Tetrachlorozincates have been used as a doping media for other transition metal ions<sup>41</sup>, particularly the cesium salt. The structures are known for the cesium salt<sup>42</sup> and the tetramethylammonium salt<sup>38</sup>. No structural studies have been done on compounds of cations capable of hydrogen bonding.

#### Purpose of Study

The synthesis and investigation of first row transition metal compounds with alkylammonium cations was undertaken as a part of a larger program, in an effort to provide the answer for the following questions:

- 1) What is the pattern of occurrence of the pseudo octahedral layer structure in the series?
- 2) What factors are responsible for the occurrence of layer structures?
- 3) Do the zinc compounds also display a variety of lattice forms which could be used as a doping media for the compounds of other transition metals, which are intensely colored so that the prime compound is unsuitable for spectral studies?

The complete crystal structure determination of all the compounds of this class would be very time consuming and expensive. Therefore, several other possible methods were explored. The X-ray powder data showed that the series contained very few isomorphous compounds, therefore, it was necessary to study some other physical property which would provide additional information. Refractive indices of most of the available compounds were measured for that purpose.

## EXPERIMENTAL

### I. Preparation of Co-ordination Compounds

A. Solvent purity. Methanol and ethanol were used exclusively in the synthesis of these compounds. Anhydrous ethanol and methanol were obtained by refluxing<sup>43</sup> reagent grade anhydrous material over magnesium turnings for twelve hours and then distilled. A convenient test capable of detecting .05% of water in the solvent was performed by adding a solution of aluminum ethoxide in benzene to a test sample of dry alcohol. A voluminous precipitate was formed if excess water was present. Commercially available anhydrous ether was used.

### B. Preparation of Anhydrous Metal(II) Chlorides.

Anhydrous metal chlorides were prepared using thionyl chloride as described by Pray<sup>44</sup>. This method has the advantage of convenience and simplicity, requiring no special apparatus. The anhydrous product was stored over drierite.

### C. Synthesis of Alkylammonium Tetrachlorometal-

lates(II). Stoichiometric quantities of anhydrous metal chloride and the appropriate alkylamine hydrochloride were dissolved in the minimum amount of dry ethanol or methanol

and anhydrous diethyl ether was diffused slowly into the above alcoholic solution. The crystals of tetrachloro-alkylammonium salts of divalent metals separated a few days later from the reaction mixture. The crystals were washed with diethyl ether and stored over dry calcium chloride. In general, they were recrystallized from the dry ethanol or methanol.

Alkylammonium Tetrachloromanganates(II). Since anhydrous manganese chloride was not very soluble in ethanol, dry methanol was used as a solvent. 0.001 Mol. of anhydrous manganese chloride was dissolved in 10 ml of methanol by heating it in a beaker covered with a water glass and then mixed with 10 ml of methanol containing .002 Mol. of the appropriate amine hydrochloride. The mixture was kept in a dessicator over anhydrous diethyl ether. The mono alkylammonium salts crystallized out as thin pink sheets, whereas the di and tetra alkylammonium salts separated as green-yellow needles. Several attempts were made to synthesize trimethylammonium tetrachloromanganate(II), but in each case pink needles of trimethylammonium trichloromanganate were obtained instead.

Alkylammonium Tetrachlorocuprates(II). Anhydrous copper chloride is fairly soluble in either solvent and no heating was necessary for dissolution. All the copper salts could be crystallized out of methanol as well as ethanol. All the monoalkylammonium salts except the isopropylammonium salt were isolated as thin yellow plates. Isopropylammonium tetrachlorocuprate(II) is green needles. Di, tri, and tetraalkylammonium salts crystallized out in a variety of morphological forms.

Alkylammonium Tetrachlorozincates(II). Some difficulties were encountered due to the extremely hygroscopic nature of anhydrous zinc chloride. The solvent used was ethanol or methanol. The metal chloride dissolved readily in the solvent. A change in the diffusion process of ether was employed. First diethyl ether was added dropwise to the alcoholic solution of stoichiometric amount of zinc chloride and alkylamine hydrochloride until the salt began to precipitate. Then a few drops of ethanol were added to redissolve the precipitate. This reaction mixture in a beaker was placed in a bigger beaker containing anhydrous diethyl ether. The large beaker was covered with a watch

glass and placed inside a dessicator overnight. Colorless needles of zinc salts were collected, dried, and stored in sealed bottles. The solvent ethanol was used in all cases except di and trimethylammonium tetrachlorozincate(II). The di- and trimethylammonium salts of zinc were synthesized out of methanol.

## II. Analytical Techniques

A. Manganese Analyses. Estimations of manganese were carried out by complexometric titrations using EDTA. The procedure is outlined by Grindley<sup>45</sup>. One molecule of EDTA forms a stoichiometric complex with one atom of the metal. Erichrome Black T was used as an indicator. The pH is critical and difficult to control in this titration. Ammonia-ammonium nitrate buffer was found to be most satisfactory.

B. Copper Analyses. Iodometric titrations using sodium thiosulfate were used for the estimation of copper. The basic method is outlined by Koltoff and Sandell<sup>46</sup>.

C. Zinc Analyses. The zinc analyses were also done by complexometric titration with the disodium salt of EDTA using the method of Grindley<sup>45</sup>. Indicator color changes were sharp and the results were very precise.

D. Halide Analyses. Halogens were quantitatively titrated against standard silver nitrate solution using dichlorofluorescein as an indicator.

Table III  
Analyses for Alkylammonium  
Tetrachloromanganates (II)

Formula	F. W.	/ Metal Calc.	/ Metal Found	/ Cl <sup>-</sup> Calc.	/ Cl <sup>-</sup> Found
$\text{Mn}(\text{CH}_3\text{NH}_3)_2\text{Cl}_4$	260.87	21.06	20.53	54.36	54.2
$\text{Mn}(\text{C}_2\text{H}_5\text{NH}_3)_2\text{Cl}_4$	288.924	19.02	19.1	49.08	48.95
$\text{Mn}(\text{n-C}_3\text{H}_7\text{NH}_3)_2\text{Cl}_4$	316.978	17.33	16.8	44.74	44.4
$\text{Mn}(\text{n-C}_4\text{H}_9\text{NH}_3)_2\text{Cl}_4$	345.032	15.92	15.84	41.1	41.0
$\text{Mn}((\text{CH}_3)_2\text{NH}_2)_2\text{Cl}_4$	288.924	19.02	18.7	49.08	49.0
$\text{Mn}((\text{CH}_3)_4\text{N})_2\text{Cl}_4$	345.032	15.92	16.2	41.1	40.98
$\text{Mn}((\text{C}_2\text{H}_5)_4\text{N})_2\text{Cl}_4$	456.248	12.04	12.1	31.08	30.9

Table IV

Analyses for Alkylammonium  
Tetrachlorocuprates (II)

Formula	F. W.	/ Metal Calc.	/ Metal Found	/ Cl <sup>-</sup> Calc.	/ Cl <sup>-</sup> Found
$\text{Cu}(\text{CH}_3\text{NH}_3)_2\text{Cl}_4$	269.472	23.58	24.0	52.62	52.65
$\text{Cu}(\text{C}_2\text{H}_5\text{NH}_3)_2\text{Cl}_4$	297.526	21.36	21.52	47.66	47.50
$\text{Cu}(\text{n-C}_3\text{H}_7\text{NH}_3)_2\text{Cl}_4$	325.58	19.52	19.6	43.55	43.6
$\text{Cu}(\text{iso-C}_3\text{H}_7\text{NH}_3)_2\text{Cl}_4$	325.58	19.52	19.35	43.55	43.58
$\text{Cu}(\text{n-C}_4\text{H}_9\text{NH}_3)_2\text{Cl}_4$	353.634	17.97	18.15	40.1	39.86
$\text{Cu}((\text{CH}_3)_2\text{NH}_2)_2\text{Cl}_4$	297.526	21.36	21.5	47.66	47.16
$\text{Cu}((\text{CH}_3)_3\text{NH})_2\text{Cl}_4$	325.58	19.52	19.63	43.55	43.45
$\text{Cu}((\text{CH}_3)_4\text{N})_2\text{Cl}_4$	353.634	17.97	18.2	40.1	40.0
$\text{Cu}((\text{C}_2\text{H}_5)_4\text{N})_2\text{Cl}_4$	464.85	13.67	13.75	30.51	30.07

Table V

Analyses for Alkylammonium  
Tetrachlorozincates (II)

Formula	F. W.	/ Metal Calc.	/ Metal Found	/ Cl <sup>-</sup> Calc.	/ Cl <sup>-</sup> Found
Zn(CH <sub>3</sub> NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub>	271.302	24.1	23.89	52.27	52.11
Zn(C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub>	299.368	21.83	21.58	47.37	47.6
Zn(n-C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub>	327.41	19.97	20.0	43.3	43.2
Zn(iso-C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub>	327.41	19.97	19.48	43.3	43.65
Zn(n-C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub>	355.464	18.39	18.22	39.89	40.1
Zn((CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> Cl <sub>4</sub>	299.356	21.84	21.94	47.37	47.42
Zn((CH <sub>3</sub> ) <sub>3</sub> NH) <sub>2</sub> Cl <sub>4</sub>	327.41	19.97	19.55	43.3	43.4
Zn((CH <sub>3</sub> ) <sub>4</sub> N) <sub>2</sub> Cl <sub>4</sub>	355.464	18.39	18.5	39.89	40.2
Zn((C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N) <sub>2</sub> Cl <sub>4</sub>	466.68	14.01	13.5	30.39	30.45

Table VI  
Densities for Standard Liquids

Liquid	Density at 25°C. (gm/ml)	$\alpha$ <sup>a</sup>
Chlorobenzene	1.10	-1.1
Carbon tetrachloride	1.60	-1.9
Methyl iodide	2.28	-2.7

a - reference 47

Table VII  
Densities of Reference Compounds

Standard Compounds	Density at 25°C. (g/ml)
Ammonium formate	1.280
Ammonium oxalate	1.500
Ammonium chloride	1.527
Sodium citrate	1.857
Sodium formate	1.920

All of the density calculations were made on DS Sigma 7 using terminal access with programs described in the Appendix A.

E. Density Measurements. Densities of the compounds were determined by a gradient tube technique. When one liquid is layered over another of greater specific gravity with which it is miscible, a linear gradient of density develops near the surface. Manipulation of a stirring rod in the graduated cylinder can extend the gradient over the greater part of the column. In the absence of convection processes the diffusion in a column of this type is so slow that the gradient will be maintained virtually unchanged for many days. A crystal introduced into such a tube settles until it reaches a level corresponding to its own density, where it remains stationary. The density gradient was calibrated by introducing crystals of known density. The immersion liquids were required to be pure and chemically inert to the compounds of interest. The table below lists the compounds used as standards and the immersion liquids with their densities.

The density at temperature  $t^{\circ}\text{C}$ . can be computed by substituting the values of density at  $25^{\circ}\text{C}$ . and in the formula:

$$d_t = d_{25} + 10^{-3} \alpha (t-25)$$

F. Refractive indices measurement. All refractive indices were measured by immersion methods.<sup>48</sup> This method of refractive index measurement employs liquids of known refractive indices as immersion media. Fragments or crystals were placed in successive immersions until by the Becke line technique it was ascertained that the refractive index of the fragment or crystal matched that of the immersion medium.

The Becke line refers to a phenomenon associated with a vertical contact of two substances of different indices of refraction observed on the stage of petrographic microscope. The Becke line is seen to the best advantage under the microscope when a medium power objective is used and the opening in the substage diaphragm is partly closed to render the incident light more nearly parallel and to reduce the total amount of illumination.

Under the microscope the Becke line may not be seen when the microscope is exactly focused on a fragment. However, if the tube of the microscope is slightly raised, a narrow line of light (Becke line) appears just inside or outside of the contact of the fragment when the microscope is raised, the fragment has a lower index than that of the

surrounding medium. Lowering the tube reverses the effect in each instance. The greater the difference in the refractive indices between the fragment and immersion medium, the greater is the displacement of the Becke line as the microscope tube is raised or lowered. This effect is illustrated in the following Figure 4.

In Figure 4(a), the objective lense is focused on the vertical contact between two substances of different refractive indices,  $N$  and  $n$ ;  $n$  is smaller than  $N$ . The light totally reflected at the contact of the medium of higher index with the medium of lower index and the light refracted into the medium of the higher index (not shown in the diagram) come to focus in the upper focal plane of the lens. Any concentration of light at the contact can not be seen. In the Figure 4(b), the microscope tube is raised slightly above the position of sharp focus. The toally reflected light (and the refracted light) now converges below the upper focal plane of the lens and in the focal plane forms a concentration near the image of the contact on the side of the medium of the higher index. In Figure 4(c), the microscope tube is lowered and the concentration of light has moved across the image of the contact into the medium of lower refractive index.

































































































































































