



Synthesis and study of some new amidine transition metal complexes
by Leo Allan Bares

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

The syntheses of five new amidine-transition metal complexes are reported. Three of these complexes, acetamidinium tetrachlorocuprate, acetamidinium tetrachlorocobaltate and acetamidinium trichloronickelate, appear to be analogous to the corresponding cesium complexes. Copper (II) acetamidinate and copper (II) benzamidinate have also been prepared.

Solution and diffuse reflectance spectra have been determined for all five complexes. Magnetic data have been obtained for the chlorocuprate, acetamidinate and benzamidinate. These data suggest possible structures, but do not allow unequivocal structural conclusions.

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SYNTHESIS AND STUDY OF SOME NEW AMIDINE
TRANSITION METAL COMPLEXES

by

LEO ALLAN BARES

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of

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Chemistry


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Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

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ABSTRACT

The syntheses of five new amidine-transition metal complexes are reported. Three of these complexes, acetamidinium tetrachlorocuprate, acetamidinium tetrachlorocobaltate and acetamidinium trichloronickelate, appear to be analogous to the corresponding cesium complexes. Copper (II) acetamidinate and copper (II) benzamidinate have also been prepared.

Solution and diffuse reflectance spectra have been determined for all five complexes. Magnetic data have been obtained for the chlorocuprate, acetamidinate and benzamidinate. These data suggest possible structures, but do not allow unequivocal structural conclusions.

INTRODUCTION

The ability of the acetate anion to function as either a monodentate or a bidentate ligand (for which there exist three possible configurations as shown in Figure 1) in complex formation with transition metals has been demonstrated (1-5). Complexes such as copper (II) acetate monohydrate, in which the bidentate nature of the acetate anion has been established (2), have evoked considerable interest in recent years. Much effort has been expended in attempting to elucidate the nature of the bonding involved in these complexes, particularly the bonding involved in the syn-syn bidentate complexes.

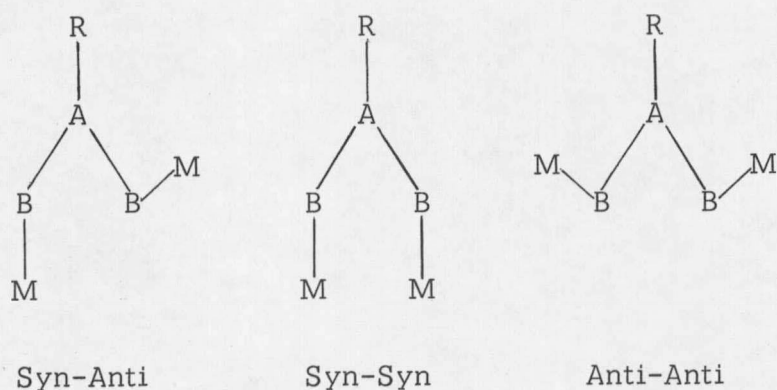


Figure 1. Bidentate Configurations

The structure of copper (II) acetate monohydrate has been determined crystallographically (2). The complex is dimeric and has a structure in which the Cu-Cu distance is 2.64 \AA (only slightly greater than the Cu-Cu distance of 2.56 \AA in metallic copper), the Cu-O distance is 1.97 \AA , and Cu is distorted out of the CuO_4 plane by 0.22 \AA .

Copper (II) acetate monohydrate exhibits an anomalously low magnetic moment of 1.42 Bohr Magnetons (compared to the spin-only value of

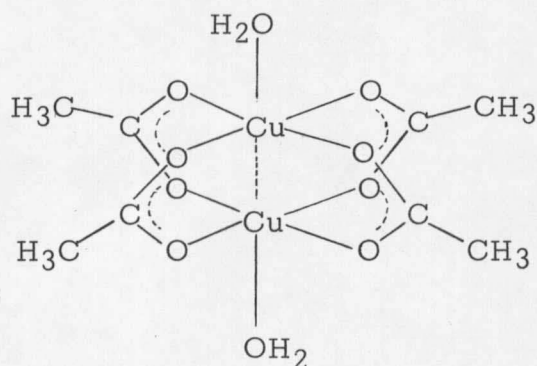


Figure 2. Structure of Copper (II) Acetate Monohydrate

1.73 B. M. normally observed for Cu (II) compounds) at room temperature and also displays an abnormal magnetic susceptibility versus temperature curve (6). Rather than decreasing with increasing temperature, as would be predicted by the Curie-Weiss law, the susceptibility increases with increasing temperature up to about room temperature. At this point the susceptibility begins to decrease. A definite maximum in the susceptibility curve, indicating antiferromagnetic behavior, is reached before adherence to the Curie-Weiss law begins. This maximum allows one to calculate a magnetic exchange energy between copper ions. The formation of a very weak δ bond between copper ions formed by $3d_{x^2-y^2}-3d_{x^2-y^2}$ orbital overlap has been postulated (6) to account for the observed exchange energy. Paramagnetic resonance spectrum studies (7) and a molecular orbital calculation (8) lend support to this type of direct exchange interaction hypothesis. Another direct exchange interaction postulate involving the formation of a strong σ bond formed by $3d_{z^2}-3d_{z^2}$ orbital overlap has also been advanced (9). Although the former explanation of the bonding involved in the copper (II)

acetate dimer has the more support, neither explanation seems to be entirely adequate.

Copper (II) formate tetrahydrate, which assumes an anti-anti configuration (10), also exhibits an anomalously low magnetic moment, having a moment of 1.64 B. M. (11).

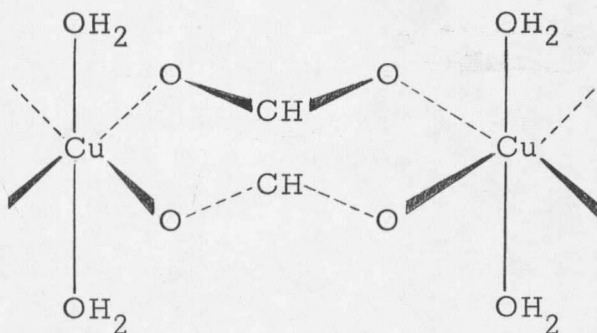


Figure 3. Copper (II) Formate Tetrahydrate

The long distance of 5.80\AA between copper ions precludes invoking a direct exchange interaction mechanism to explain this stronger-than-normal magnetic interaction. A super exchange via a π pathway established by the $3d_{yz}$ or $3d_{xz}$ orbitals of the copper ion and the $2p_{\pi}$ orbitals of the bridging formate group has been suggested to explain the observed interaction (12). A similar pathway may also be constructed for the copper (II) acetate dimer and super-exchange may then be considered as a possible mechanism for its interaction. A combination of direct and super exchange may also be considered as a possible mechanism in this case. The precise nature of the metal-metal bond in the syn-syn bidentate complexes, assuming one, in fact, exists, remains an interesting and unsolved problem. The present project is part of a larger program designed to help solve this problem.

1,3-Diphenyltriazenidocopper(I) has a syn-syn bidentate structure very similar to that of copper (II) acetate, but the structure of the Cu (II) complex has not been determined unequivocally. It has been assumed, however, that the structure is also a syn-syn dimer (13). 1,3-Diphenyltriazenido Cu(II) has been reported to be diamagnetic at room temperature (13). Presumably, increased magnetic interaction may be due to one of, or a combination of, at least two factors. A decreased metal-metal distance would allow more extensive orbital overlap and consequently greater magnetic interaction would occur. A more strongly electron releasing ligand should increase the metal orbital electron density and thereby also increase the orbital overlap.

The preparation and study of transition metal complexes employing ligands other than, but geometrically similar to, acetate may well provide information in understanding the nature of the metal-metal bonding in copper(II) acetate and the complexes which exhibit similar, abnormal magnetic properties. It may be possible to synthesize a series of syn-syn bidentate dimers which have structures intermediate to copper(II) acetate and 1,3-Diphenyltriazenidocopper (II). For example, the substitution of nitrogen for one acetate oxygen and then substitution of nitrogen for both oxygens would provide such a series. A series of this type should provide magnetic information which would augment understanding of the magnetic interactions and metal-to-metal bonding in these compounds.

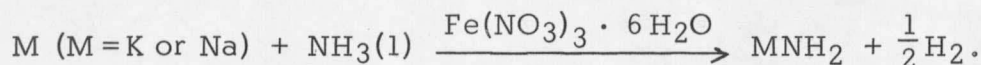
The amidines, which are nitrogen analogs to the alkanoates, have been selected as one type of ligand to employ in this effort. It is the

purpose of the present work to synthesize, in particular, Cu (II) acetamidate and to perform preliminary investigation of the complex.

EXPERIMENTAL

Preparation of Sodium and Potassium Amide

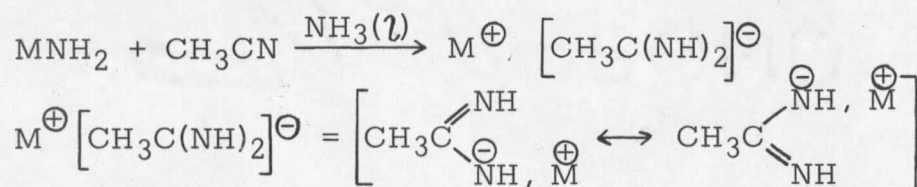
Potassium or sodium amide can be prepared by the action of potassium or sodium metal on liquid ammonia using ferric nitrate hexahydrate as the catalyst (14):



The procedure followed in the above preparations is essentially that of Greenlee and Henne (14) with the exception that additional drying precautions were observed. Drying was effected by withdrawing liquid ammonia from an inverted commercial cylinder into a large (3-5 liter) three-necked flask, which was insulated and had one neck fitted with a two-foot drying tube to be attached later to a reaction flask. When the flask was half-filled with liquid ammonia, five to fifteen grams of cut sodium metal were introduced through the third neck. After the ammonia had been in contact with the sodium metal for five to eight hours, it was passed through the drying tube containing KOH into a one-liter reaction flask where it was condensed by a dry ice-acetone condenser. The procedure described by Greenlee and Henne was then adhered to closely.

Attempts to Prepare Sodium and Potassium Acetamidinate

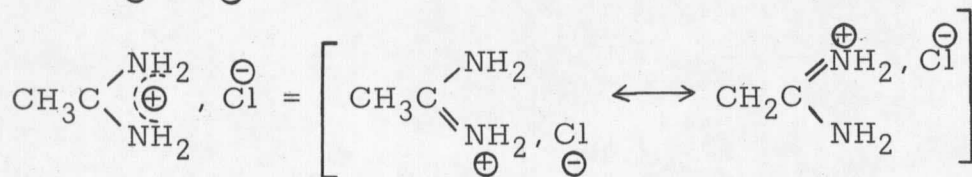
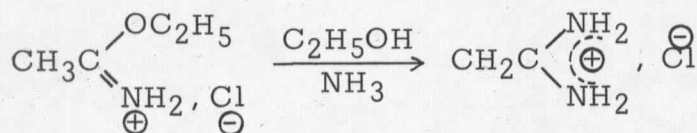
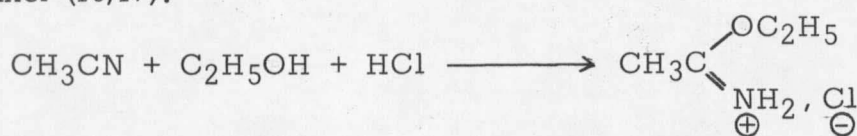
Cornell (15) describes the preparation of the sodium and potassium salts of acetimidine by the reaction between sodium or potassium amide and acetonitrile in liquid ammonia:



Reactions employing both sodium and potassium were attempted several times with variations in the rate of addition of reactants and by reversing the order of addition. Invariably, the product was a reddish-brown solid which became very hard upon sitting and which was insoluble in water, ethanol, acetonitrile and dilute hydrochloric acid. These observations suggest that considerable polymerization occurs rather readily. The sodium reaction seems to be more susceptible to polymerization than does the potassium reaction. Commercial sodium amide, which does not seem to be as reactive as the sodium amide prepared by the method of Henne and Greenlee, gives very poor results in the above addition. The lesser reactivity of the commercial sodium amide is probably due to its lower purity and to the fact that the compound is shipped under mineral oil, which is rather difficult to remove completely.

Synthesis of Acetamidinium Chloride

Acetamidinium chloride is most conveniently prepared by the method of Pinner (16,17):



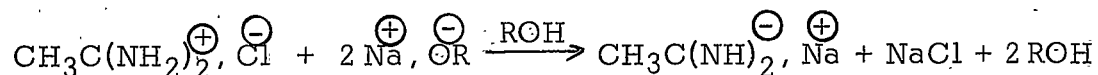
Dry hydrogen chloride gas is passed into a solution of acetonitrile and ethanol to form the acetimido ethyl ether hydrochloride, which is then treated

with an ammoniacal-alcohol solution to form the acetamidinium chloride. The yield of pure acetamidinium chloride after two recrystallizations from dried absolute ethanol is 65 to 70% of the theoretical yield.

There exists a discrepancy in the literature on the melting point of this substance. The Handbook of Chemistry and Physics (18) lists a melting point of 166-167°C for acetamidine. Dox (16) reports a melting point of 164-166, Pinner (17) reports 166-167, and Lange's Handbook of Chemistry (19) lists a melting point of 177° for acetamidinium chloride. Hammond and Neuman (20) give a melting point of 165-168° for the same compound. Acetamidinium chloride synthesized in this laboratory melts at 175-176° and a sample of the compound obtained from Eastman-Kodak Company melted at 174-177°.

Attempts to Convert Acetamidinium Chloride to Sodium Acetamidinate

It seemed reasonable that this conversion could be effected by reacting acetamidinium chloride with a sodium alkoxide using the corresponding alcohol as the solvent:



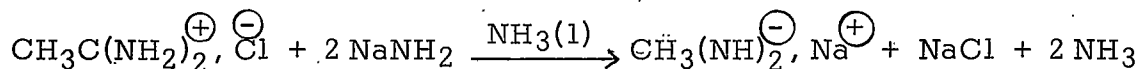
However, the systems employing ethanol, 1-propanol and 1-butanol failed to produce satisfactory results.

The sodium alkoxides readily remove hydrogen chloride from acetamidinium chloride. Sodium ethoxide, however, reacted no farther, as evidenced by a neutralization test with standard acid, and is apparently not a strong enough base to abstract an amidine proton.

Although the final products from the sodium propoxide and sodium butoxide reactions were not isolated, reaction with CuCl_2 (2:1 molar ratio) in

situ produced ill-defined green compounds. Subsequent nitrogen analyses proved that none of these compounds was the desired copper acetamidinate. No further attempts were made to characterize them.

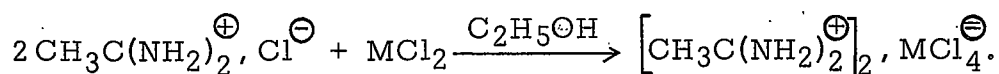
The analogous reaction with sodium amide,



yielded the same type of product as was observed to form from the reaction between sodium amide and acetonitrile. Consequently, it was concluded that this reaction, also, resulted in too much polymerization to be useful.

Synthesis of $[\text{CH}_3\text{C}(\text{NH}_2)_2]_2^{\oplus} \text{MCl}_4^{\ominus}$ (M = Cu, Co)

The new compounds $[\text{CH}_3\text{C}(\text{NH}_2)_2]_2^{\oplus} \text{MCl}_4^{\ominus}$, where M = Cu and Co, have been prepared according to the following equation:



Anhydrous metal chloride (21) and acetamidinium chloride were mixed in a molar ratio of 2:1 in dried absolute ethanol (22). The metal chloride was first dissolved in absolute ethanol and then acetamidinium chloride was added to this solution. When both reactants had dissolved, the solutions were placed in a desiccator over anhydrous ether. Well-formed crystals grew slowly as the solutions became saturated with ether. After crystallization, the crystals were filtered away from the solution, and dried in a vacuum desiccator over concentrated sulfuric acid. The crystals are only slightly deliquescent; however, to insure exclusion of moisture, they were stored in tightly-stoppered bottles.

The copper complex is an intense golden yellow platelet crystal. It decomposes at 108-110° in the atmosphere.

Analysis: %Cl, 44.0, %N, 17.2; %Cu, 19.7

Calculated composition of acetamidinium tetrachlorocuprate:

%Cl, 43.8; %N, 17.3; %Cu, 19.7.

The cobalt complex prepared in this manner forms as dark blue needle-like crystals which melt at 207-209° in the atmosphere.

Analysis: %Cl, 44.5; %N, 17.3; %Co, 18.4.

Calculated percentage composition of acetamidinium tetrachlorocobaltate: %Cl, 44.5; %N, 17.6; %Co, 18.5.

Chloride was determined by the adsorption indicator method (23), copper was determined iodometrically (24), nitrogen was determined by the Kjeldahl method (25), and cobalt was determined by complexometric titration with ethylenediaminetetraacetic acid (26).

All ultraviolet and visible solution spectra reported in this thesis were recorded at room temperature by a Beckman DK-2 spectrophotometer. The spectra of acetamidinium tetrachlorocuprate and acetamidinium tetrachlorocobaltate in acetonitrile are shown in Figures 4, 5, 6 and 7. Absorption bands and molar absorptivities of these spectra are listed in Table 1.

Diffuse reflectance spectra at room temperature of the crystalline chlorocuprate and chlorocobaltate (Figures 8 and 9) and of complexes to be discussed subsequently were run on a Beckman Model B spectrophotometer. Special accessories used for reflectance measurements include a Beckman #12400 integrating sphere reflectance attachment and a 2000 megohm photo-tube resistor. Magnesium carbonate was used as a reflectance standard for the chlorocobaltate. Because of the high intensity of absorption in the

chlorocuprate, magnesium carbonate was found to be an unsuitable standard. In this case, the chlorocobaltate was used as the standard.

The infrared spectra of the tetrachloro complexes milled in nujol and fluorolube were taken with a Beckman IR-5A spectrophotometer. The spectra are identical with each other and essentially identical to that of acetamidinium chloride. Spectral bands were observed at 1060, 1100, 1150, 1360, 1460, 1650, 3150 and 3200 wavenumbers. Assignments of these bands will be made in the discussion.

Magnetic susceptibilities reported in this paper were determined at 80°K, 196°K and 298°K by Miss Karen Diamond. A Gouy balance, consisting of a Mettler analytical balance, a Harvey-Wells Model L-44V electromagnet and a Magnion Model #HS 425 power supply, was used to make the measurements. The electromagnet used had 4" pole caps with a variable gap. A gap of 1.5" was employed in all determinations. Temperatures of 80°K and 196°K were obtained from liquid air and dry ice-acetone baths. The baths in which the 6 mm. Gouy tube was suspended were contained in a specially designed Dewar-type flask. Magnetic field strengths were determined by using $\text{HgCo}(\text{CNS})_4$ (27) as a magnetic standard.

Magnetic data for acetamidinium tetrachlorocuprate are listed in Table II. Pascal's constants (28) have been used for diamagnetic corrections to the susceptibilities determined and are included in the susceptibilities listed in the table. No measurements were made on acetamidinium tetrachlorocobaltate at this time.

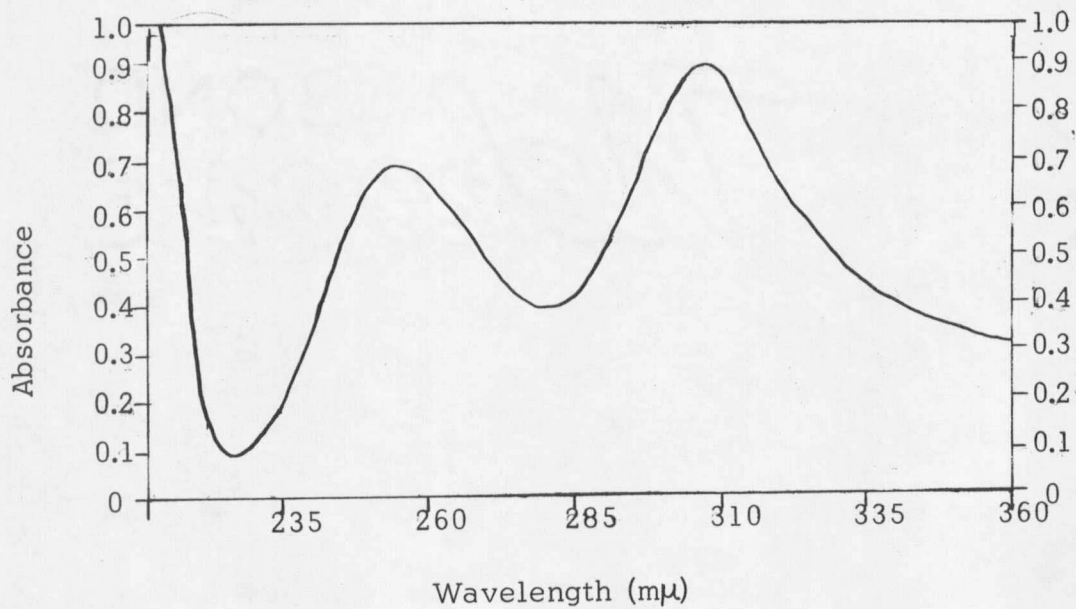


Figure 4. Ultraviolet Spectrum of Acetamidinium Tetrachlorocuprate

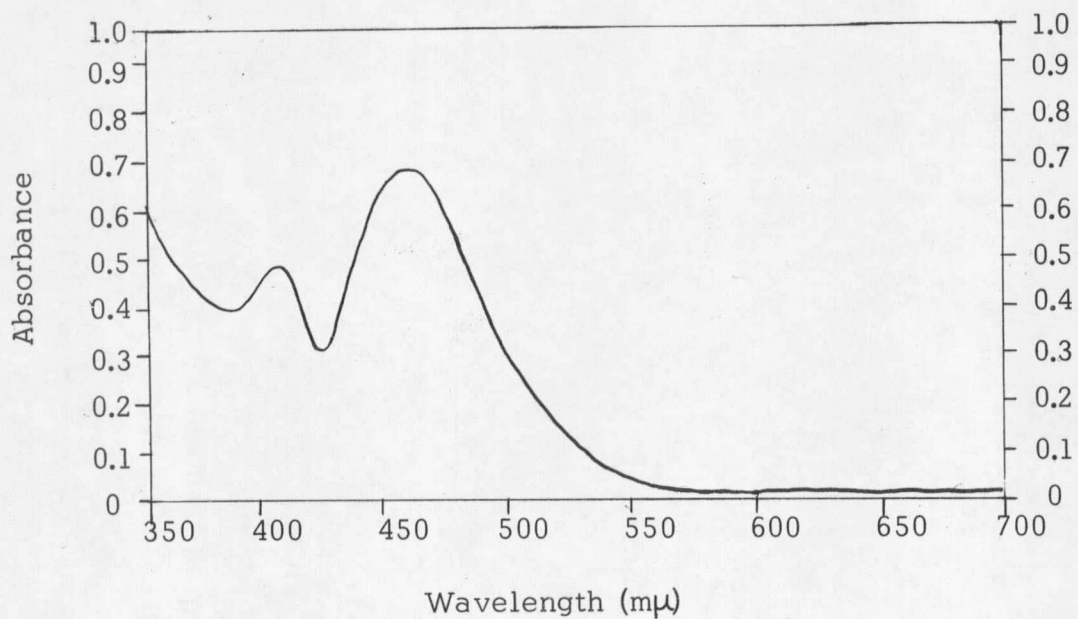


Figure 5. Visible Spectrum of Acetamidinium Tetrachlorocuprate

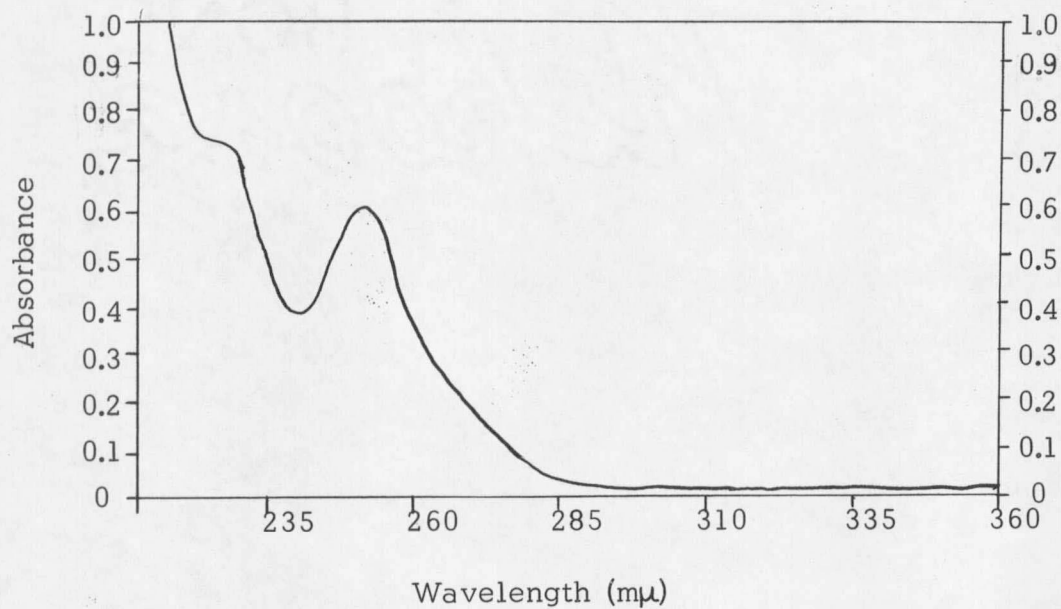


Figure 6. Ultraviolet Spectrum of Acetamidinium Tetrachlorocobaltate

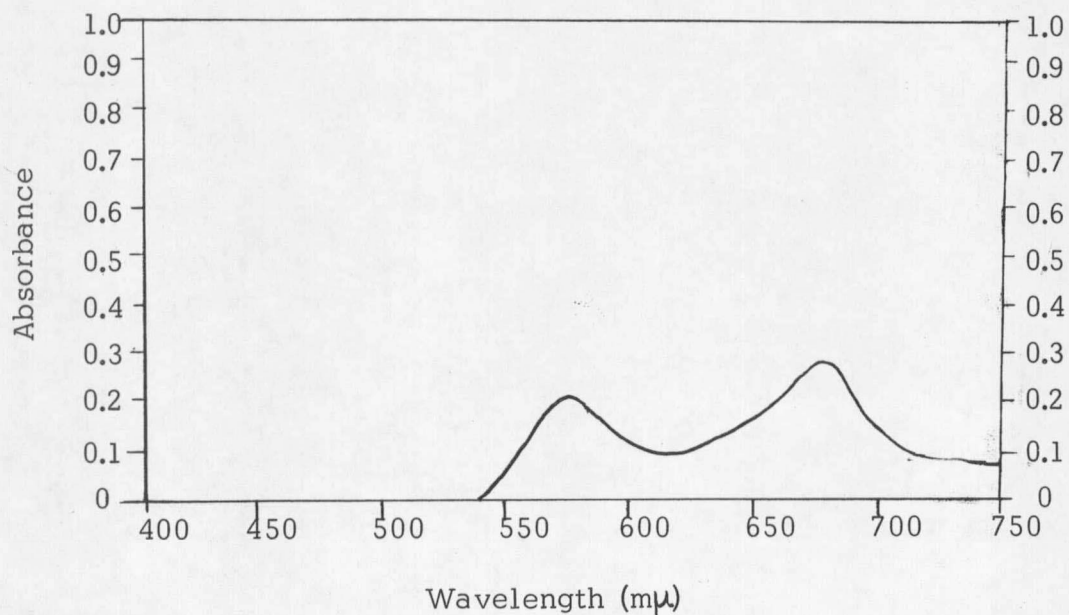


Figure 7. Visible Spectrum of Acetamidinium Tetrachlorocobaltate

TABLE I

Spectral Bands and Intensities of $[\text{CH}_3\text{C}(\text{NH}_2)_2]^{\oplus}_2, \text{MCl}_4^{\ominus}$

Complex	Concentration	Absorption Wavelength (m μ)	Path length of radiation (cm.)	Molar Absorptivity
Cuprate	2.31×10^{-3} M	255	0.1	3000
		307	0.1	4100
		380	0.2	950
		453	0.2	1450
Cobaltate	2.30×10^{-3} M	227 (shoulder)	0.1	-----
		252	0.1	2450
		673	0.2	520
		579	0.2	300

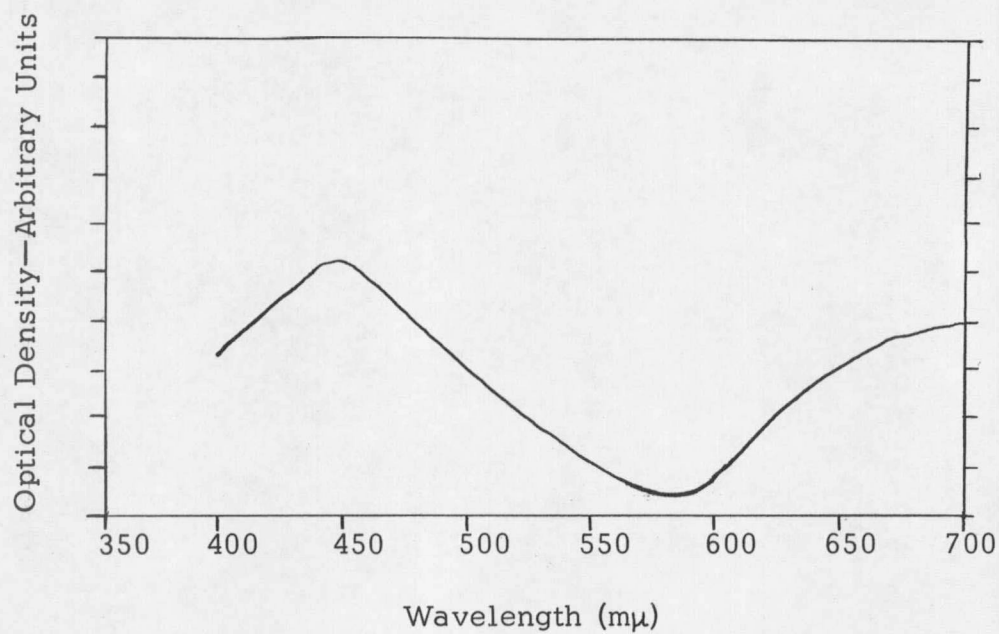


Figure 8. Diffuse Reflectance Spectrum of Acetamidinium Tetrachlorocuprate

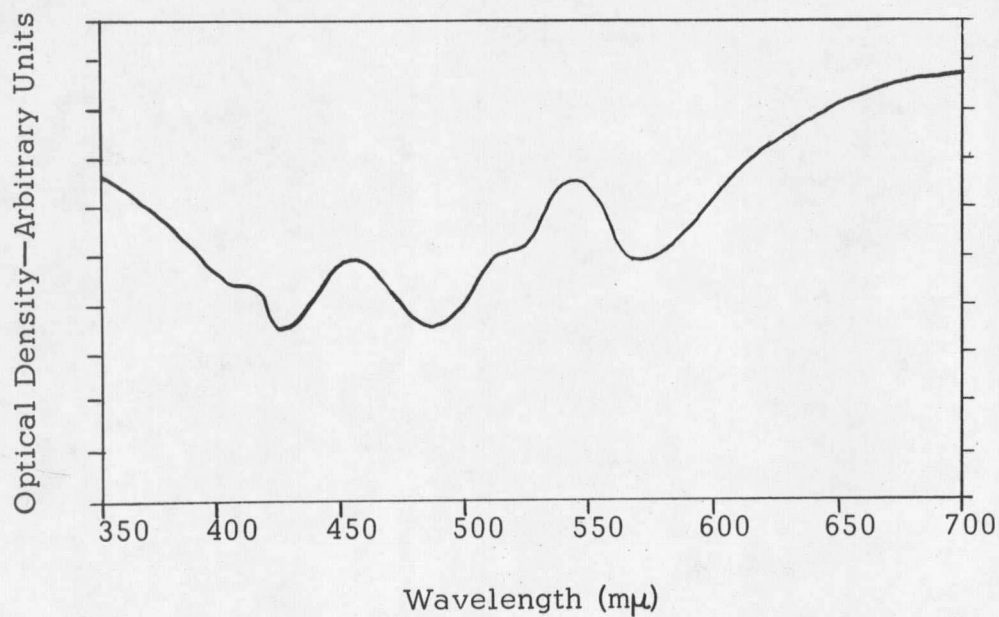


Figure 9. Diffuse Reflectance Spectrum of Acetamidinium Tetrachlorocobaltate

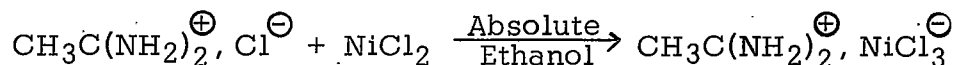
TABLE II

Magnetic Data on $[\text{CH}_3\text{C}(\text{NH}_2)_2]^+\text{CuCl}_4^-$

Temperature ($^{\circ}\text{K}$)	χ_M (cgs, emu) $\times 10^6$ Magnetic Susceptibility	(B. M.) Magnetic Moment
80	5577	1.93
196	2462	1.92
298	1643	1.98

Preparation of Acetamidinium Trichloronickelate

Nickel chloride does not react with acetamidinium chloride in the same manner as does CuCl_2 and CoCl_2 . Under the same conditions that CuCl_2 and CoCl_2 react with $\text{CH}_3\text{C}(\text{NH}_2)_2^{\oplus}, \text{Cl}^{\ominus}$ to form the tetrachlorometalate complexes, NiCl_2 reacts to form the trichloro complex.



Acetamidinium chloride and anhydrous nickel chloride were mixed in a 1:1 molar ratio in anhydrous ethanol. Slow addition of ether, by the method already described, to the resulting yellowish-green solution precipitated dark orange, feather-like crystals. The crystals are very hygroscopic and must be protected from the atmosphere.

Analysis: % Cl, 47.4; % N, 12.5; % Ni, 26.1.

Calculated from $\text{CH}_3\text{C}(\text{NH}_2)_2^{\oplus}, \text{NiCl}_3^{\ominus}$: % Cl, 47.5; % N, 12.5; % Ni, 26.1.

Chloride and nitrogen were determined by the adsorption indicator and Kjeldahl methods respectively. Nickel was determined by complexometric titration with EDTA (29).

Infrared spectra of acetamidinium trichloronickelate mulled in nujol and fluorolube show the same bands as the tetrachlorocuprate and cobaltate complexes.

The solution spectrum of the trichloronickelate in absolute ethanol from 360 to 1000 $\text{m}\mu$ is shown in Figure 10. The spectrum was run with a NiCl_3^{\ominus} concentration of 3.49×10^{-2} M. One cm. cells were used. No absorption was observed between 250 and 360 $\text{m}\mu$.

The diffuse reflectance spectrum of crystalline acetamidinium trichloronickelate using magnesium carbonate as a reflectance standard is shown in Figure 11.

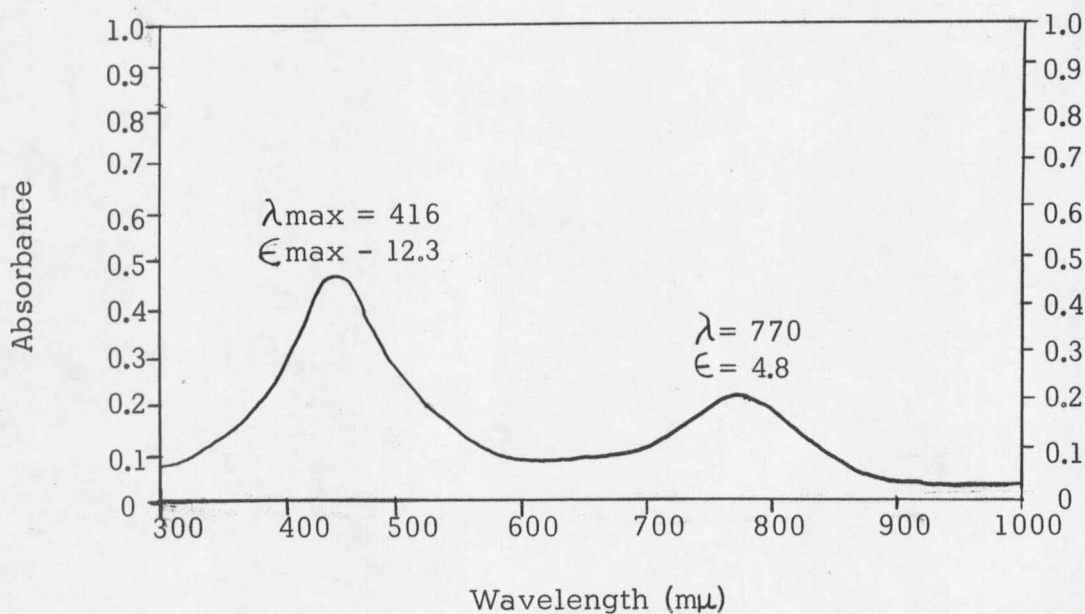


Figure 10. Solution Spectrum of $\text{CH}_3\text{C}(\text{NH}_2)_2^+$, NiCl_3^-

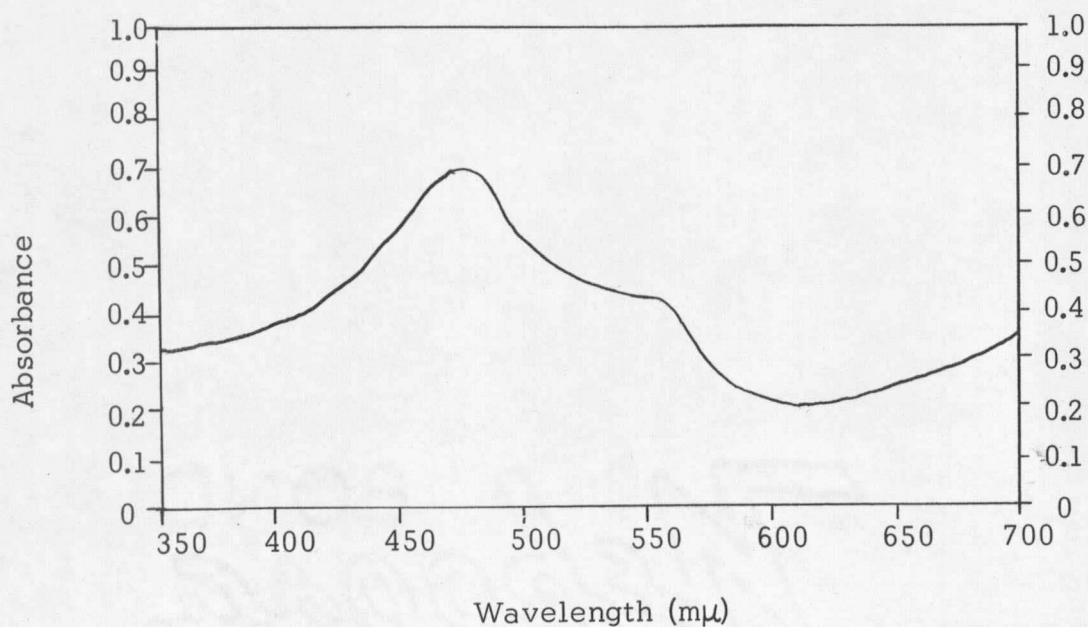
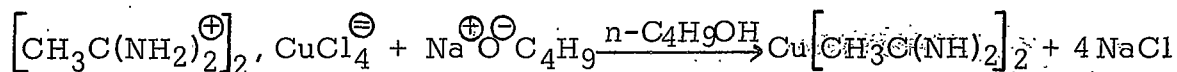


Figure 11. Diffuse Reflectance Spectrum of $\text{CH}_3\text{C}(\text{NH}_2)_2^+$, NiCl_3^-

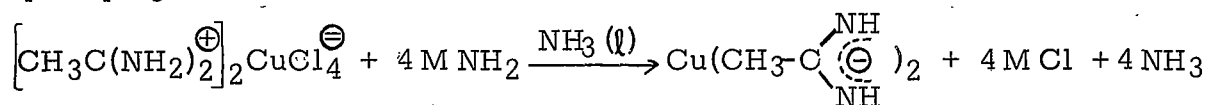
Synthesis of Copper (II) Acetamidinate

After acetamidinium tetrachlorocuprate had been synthesized, it provided a new avenue for possible synthesis of Cu (II) Acetamidinate. Removal of four molecules of hydrogen chloride from $[\text{CH}_3\text{C}(\text{NH}_2)_2]^{\oplus}_2$, CuCl_4^{\ominus} might yield the desired product, if the removal could be effected without completely decomposing the chlorocuprate. With this in mind, it was decided that sodium butoxide, a reasonably strong base, might be effective in removing the HCl, while leaving the acetamidinate moiety intact.



Sodium butoxide was prepared by refluxing cut and dried sodium metal in excess reagent grade 1-Butanol for about an hour. This solution was then added slowly to a solution of acetamidinium tetrachlorocuprate in 1-Butanol. The reactants, sodium butoxide and the chlorocuprate, were mixed in a 4:1 molar ratio. A white precipitate, later identified as predominantly sodium chloride, began to form immediately. Simultaneously, the solution turned dark blue. When precipitation seemed to be complete, the solution was filtered. The solvent was then removed from the solution by high vacuum. This procedure left a gum which failed to crystallize, so the reaction was repeated to the point of vacuum distillation. Rather than removing the 1-Butanol under vacuum, various non-polar solvents, including ether, carbon tetrachloride, p-dioxane and hexane, were added to the filtrate in an attempt to precipitate the blue constituent. The only effect observed in all cases was an alteration in the color of solution. At this point, investigation of the system was discontinued.

The metal amides are sufficiently strong bases to remove 4 molecules of hydrogen chloride and one would expect to encounter no difficulty in removing the final product from liquid ammonia. The problem is that the amides are also strong enough bases to produce undesirable side reactions with the acetamidinate. These side reactions, however, might be inhibited by varying the reaction conditions.



Sodium amide was prepared as described previously. A stoichiometric quantity of tetrachlorocuprate was added to the sodium amide-liquid ammonia mixture. Within a short time, the contents of the reaction flask had turned green. However, after about an hour the solution had turned brown. When the ammonia had completely evaporated, a hard reddish-brown residue, very much like that observed to form in the $\text{NaNH}_2\text{-CH}_3\text{CN}$ reaction, remained.

The use of potassium amide was much more fruitful. Again, the KNH_2 was prepared by the method of Greenlee and Henne with the added precaution of drying the ammonia¹. After the KNH_2 had been prepared in the dried ammonia, the cuprate complex was added. The stoichiometric quantity was added in toto to the well-stirred mixture to avoid as many undesirable side reactions as possible. The dark green color of the ammonia solution persisted in this case until evaporation was complete. Again, much reddish-brown residue remained; however, this was interspersed by a dark green residue. Absolute ethanol was then added to this mixed residue. Within

1. The drying of the ammonia seems to be very critical. In all cases in which this was neglected, results similar to those of the sodium reaction were obtained.

three-four hours, the ethanol had assumed a dark blue color. This mixture was periodically shaken over a period of eight to twelve hours to extract as much of the green residue as possible. The solution was then filtered and the ethanol was allowed to evaporate in the atmosphere. When nearly all the ethanol had evaporated, dark blue crystals had formed. These were filtered away from the ethanol and dried over concentrated sulfuric acid in vacuo for twelve hours.

The crystals were rewashed with dry ethanol, redried in vacuo, and heated in an oven at 80-85° for one hour. This procedure brought the number of molecules of solvation quite close to one. Yields were from 20-30%.

Final analysis: % Cu, 37.8; % N, 24.5.

Calculated for $\text{Cu}[\text{CH}_3\text{C}(\text{NH})_2]_2 \cdot 1 \text{EtOH}$: % Cu, 28.4; % N, 25.0.

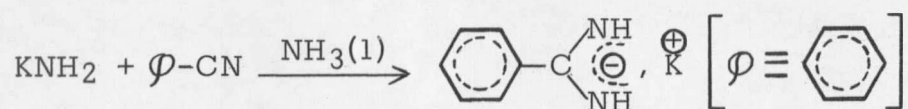
The blue crystals are insoluble in most of the common cryoscopic and ebullioscopic solvents. The only solvents found in which they were soluble were ethanol and dimethyl sulfoxide. Heating the ethanol-Cu(II) Acetamidinate solution to the boiling point of ethanol decomposed the amidinate. No cryoscopic or ebullioscopic data on DMSO are presently available. Consequently, no molecular weight determination was made on Cu(II) Acetamidinate.

Solution spectra of $\text{Cu}(\text{II})[\text{CH}_3\text{C}(\text{NH})_2]_2 \cdot 1 \text{EtOH}$ in DMSO are shown in Figures 12 and 13. Absorption bands and molar absorptivities for the complex are reported in Table III. The diffuse reflectance spectrum of the crystalline acetamidinate using magnesium carbonate as a reflectance standard is shown in Figure 14. An infrared spectrum of Cu(II) Acetamidinate in a KBr micropellet is shown in Figure 15. Magnetic data for this complex are

listed in Table IV. Pascal's constants have been included in the susceptibilities shown.

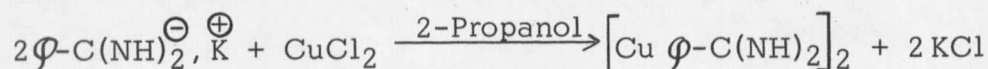
Synthesis of Copper (II) Benzamidinate

Potassium benzamidinate is much more readily prepared than potassium acetamidinate. The salt was made by reacting potassium amide with double-distilled benzonitrile in dried liquid ammonia.



Yields of 50-70% were obtained from this reaction.

The potassium benzamidinate prepared by this procedure was then reacted with anhydrous CuCl_2 in a 2:1 molar ratio.



CuCl_2 was first dissolved in isopropyl alcohol and to this solution the appropriate quantity of potassium benzamidinate was added. Potassium benzamidinate is essentially insoluble in isopropyl alcohol. When it was added to the CuCl_2 solution, the resultant mixture turned dark green. After a half-hour of stirring, the mixture had turned canary yellow. This yellow material was filtered away from the isopropyl alcohol and placed in ethanol. The ethanol gradually assumed a bluish-purple color. After ten hours of stirring this mixture, the blue ethanol solution was filtered away and placed in an evaporating dish exposed to the atmosphere.

Purple crystals formed as the ethanol evaporated. These were washed several times with cold absolute ethanol, dried over concentrated sulfuric acid in vacuo, and finally dried in an oven at 80°C for one hour. Yields of 15-20% were obtained.

Analysis: % Cu, 18.5; % N, 16.3.

Calculated for $\text{Cu}[\text{C}(\text{NH}_2)_2]_2 \cdot 1 \text{EtOH}$: % Cu, 18.4; % N, 16.1.

The benzamidinate complex decomposes at 170-175°C. Heating above 120° for prolonged periods removes ethanol of solvation.

Cu (II) benzamidinate is insoluble in the same solvents in which copper (II) acetamidinate is insoluble.

Solution spectra of copper (II) benzamidinate in DMSO are shown in Figures 16 and 17. Absorption bands and molar absorptivities are listed in Table III. The diffuse reflectance spectrum using magnesium carbonate as a standard is shown in Figure 18.

Magnetic data for this complex are recorded in Table IV. Pascal's diamagnetic corrections are included in the susceptibilities.

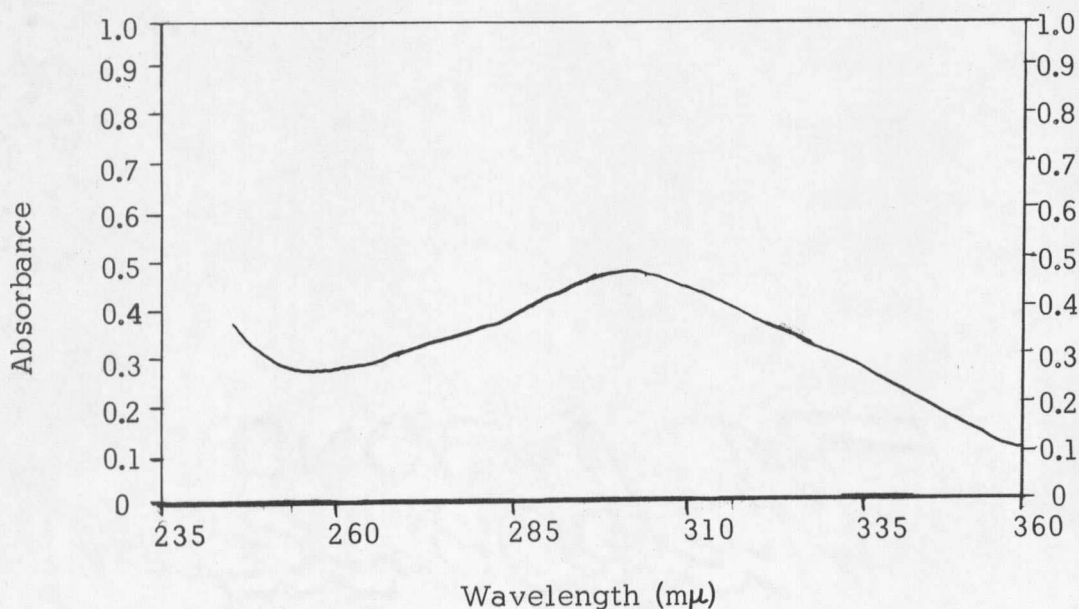


Figure 12. Ultraviolet Spectrum of $\text{Cu}[\text{CH}_3\text{C}(\text{NH}_2)_2]_2 \cdot \text{EtOH}$

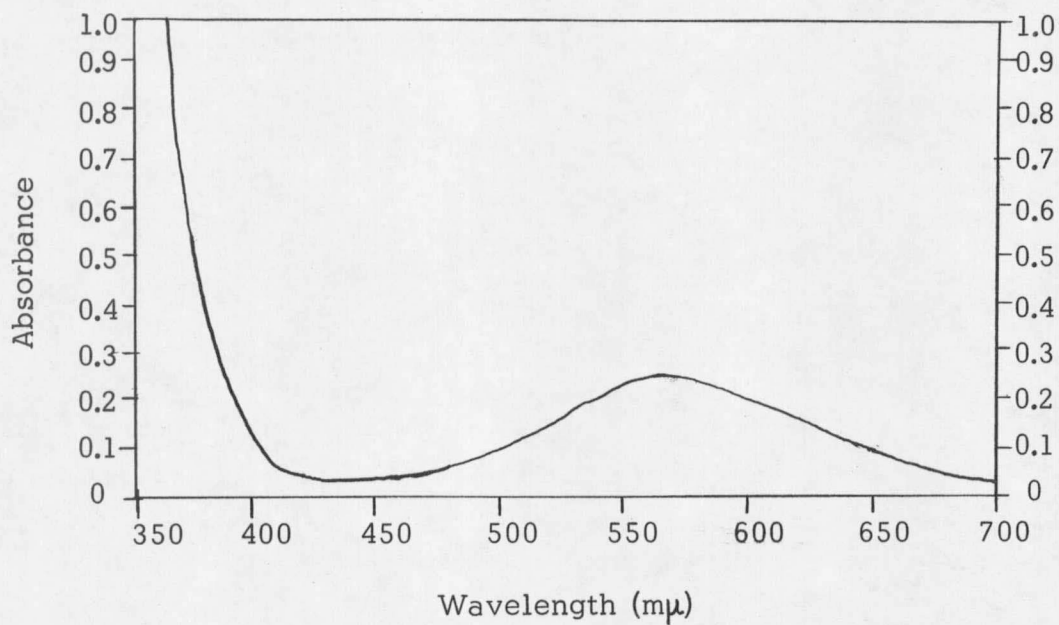


Figure 13. Visible Spectrum of $\text{Cu}[\text{CH}_3\text{C}(\text{NH})_2]_2 \cdot \text{EtOH}$

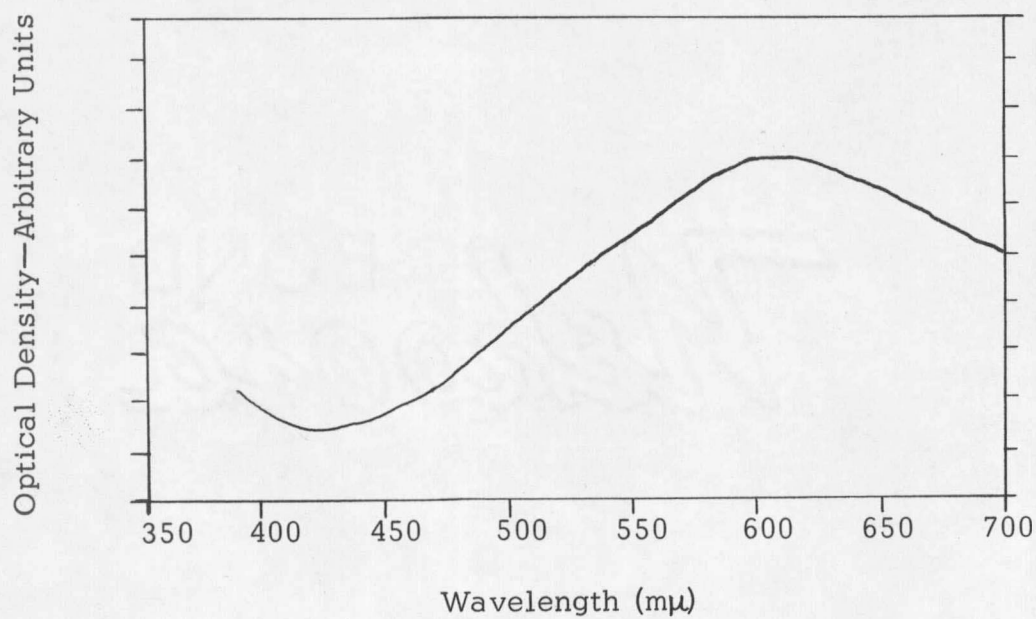


Figure 14. Reflectance Spectrum of $\text{Cu}[\text{CH}_3\text{C}(\text{NH})_2]_2 \cdot \text{EtOH}$

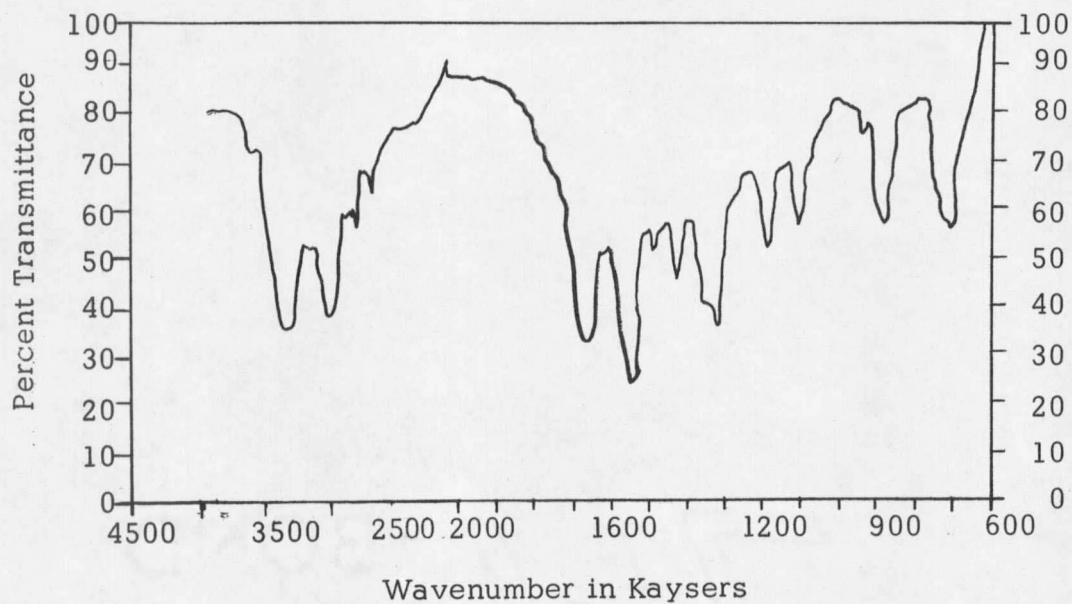


Figure 15. Infrared Spectrum of $\text{Cu}[\text{CH}_3\text{C}(\text{NH})_2]_2 \cdot \text{EtOH}$

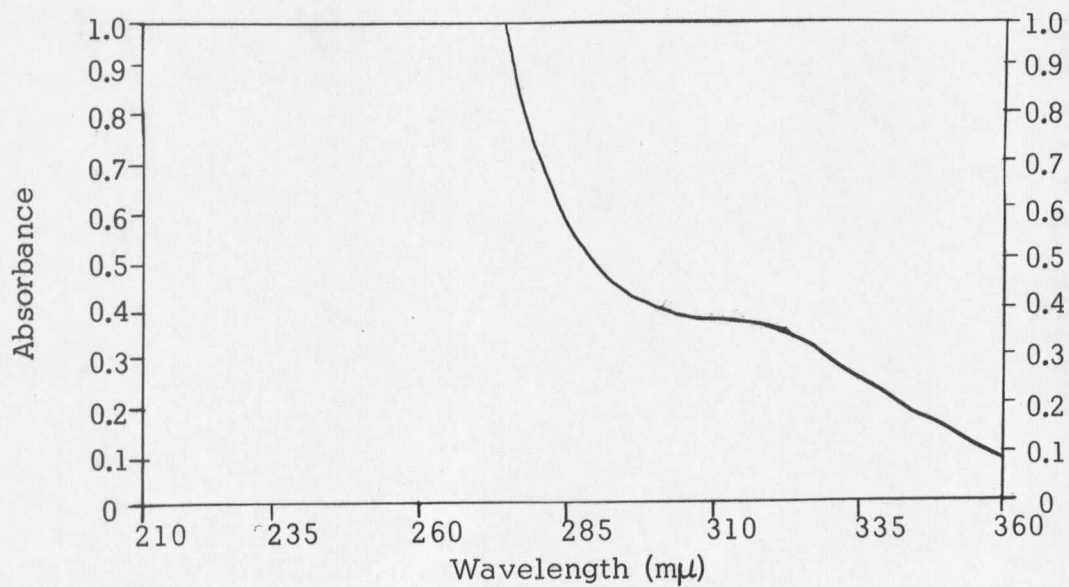


Figure 16. Ultraviolet Spectrum of $\text{Cu}[\phi\text{C}(\text{NH})_2]_2 \cdot \text{EtOH}$

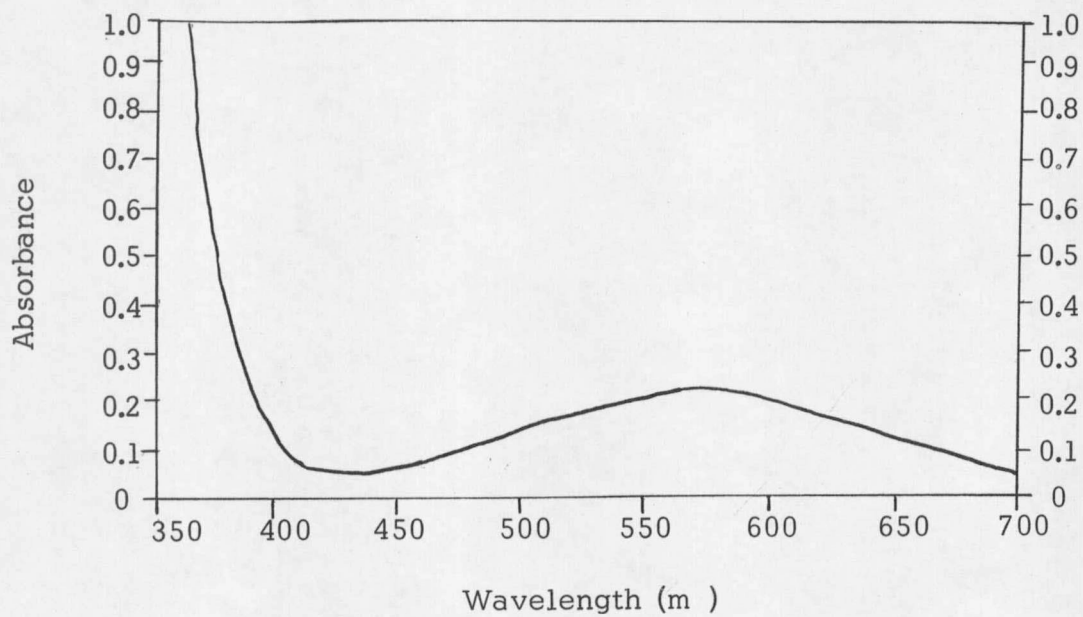


Figure 17. Visible Spectrum of $\text{Cu}[\text{9C}(\text{NH})_2]_2 \cdot \text{EtOH}$

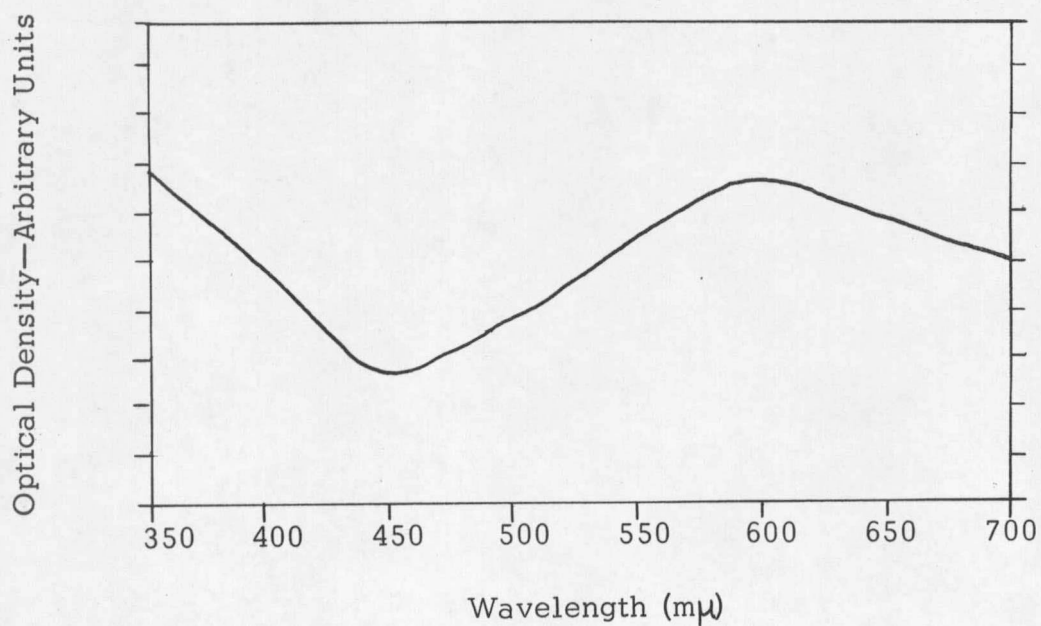


Figure 18. Reflectance Spectrum of $\text{Cu}[\text{9C}(\text{NH})_2]_2 \cdot \text{EtOH}$

TABLE III

Spectral Bands and Spectral Intensities of Copper (II) Amidinates

Compound	Concentration in DMSO	Absorption Wavelength (m μ)	Pathlength of Radiation (cm.)	Molar Absorptivity
Acetamidinate	1.8×10^{-3} M	302	0.1	2610
		570	1.0	93
Benzamidinate	9.8×10^{-4} M	300 (shoulder)	0.1	----
		578	1.0	133

TABLE IV

Magnetic Data on Copper (II) Amidinates

Compound	Temperature (°K)	χ_M (cgs, emu) $\times 10^6$ Magnetic Susceptibility	μ (B.M.) Moment
Acetamidinate	80	5546	1.89
	196	2291	1.90
	297	1470	1.89
Benzamidinate	80	5883	1.94
	196	3078	2.19
	297	2140	2.26

DISCUSSION

Acetamidinium Tetrachlorocuprate

The chlorocuprate exhibits a fairly strong ($\epsilon = 1450$ in solution spectrum) absorption band at about $450 \text{ m}\mu$ ($22,200 \text{ cm.}^{-1}$ in both its crystalline and acetonitrile spectra). All of the known CuCl_4^{\ominus} complexes show a charge transfer band in this region. Cs_2CuCl_4 , known to have a distorted tetrahedral structure (30), shows a charge transfer band at $24,800 \text{ cm.}^{-1}$ (31) at 77°K . $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$, a square planar structure (32), exhibits a charge transfer band at $24,900 \text{ cm.}^{-1}$ (33). CsCuCl_3 has a distorted octahedral layer structure in which each copper ion is surrounded by four nearest chlorides. This complex has a charge transfer band at $24,600 \text{ cm.}^{-1}$ (33). Smith and Griffiths (34) report a band at $22,200 \text{ cm.}^{-1}$ for CuCl_2 in a melt of tributyl-2,4-dichlorobenzylphosphonium chloride. They consider this band and the d-d band at 8000 cm.^{-1} as criteria for tetrahedral CuCl_4^{\ominus} . The fact that the square planar structures exhibit similar bands, however, renders an unequivocal structural conclusion, on this basis alone, difficult if not impossible.

The magnetic moment of the cuprate complex over the temperature range $80\text{--}298^\circ\text{K}$ appears to be essentially temperature independent, characteristic of magnetically dilute complexes. Although only three points were obtained, a plot of susceptibility versus temperature suggests that the complex follows the Curie-Weiss Law in the $80\text{--}298^\circ\text{K}$ temperature range. A low Weiss constant of about -12° is obtained by plotting $(\chi_M)^{-1}$ versus T . CuCl_2 , which is antiferromagnetic with a critical temperature of 70°K (35), has a structure in which Cu is bridged by two Cl's (36). LiCuCl_3 dihydrate and KCuCl_3 also have chloride bridged structures and show antiferromagnetic

behavior (37). All these factors tend to indicate that acetamidinium tetrachlorocuprate is not antiferromagnetic and does not contain copper bridged by two chlorides.

Figgis and Harris (38) list a moment of 2.00 for Cs_2CuCl_4 and suggest that the magnetic moments of tetrahedral copper complexes may be higher than the moments for square planar complexes. $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$ has a moment of 1.77 (33). Acetamidinium tetrachlorocuprate has a room temperature moment of 1.98.

On the basis of the evidence available at the present time, $[\text{CH}_3\text{C}(\text{NH}_2)_2]^+\text{CuCl}_4^-$ probably does not have an isolated square planar structure. The present evidence seems to indicate a tetrahedral structure.

All of the infrared absorption bands listed on page 12 may be assigned to the acetamidinium cation. The fact that the infrared spectra of acetamidinium chloride and acetamidinium tetrachlorocuprate are identical suggests that the cuprate complex contains the acetamidinium cation and not a coordinated acetamidinium species.

Acetamidinium Tetrachlorocobaltate

Ferguson (39) has reported the crystal field spectrum of CoCl_4^- in several crystalline environments. He points out that the visible absorption bands for the distorted tetrahedral CoCl_4^- fall into three main regions, 14000 to nearly 17000 cm^{-1} , 17,200 to a little more than 20,000 cm^{-1} , and 22,000 to a little above 24,000 cm^{-1} . The diffuse reflectance spectrum of acetamidinium tetrachlorocobaltate has bands at 23,800, 22,200, 19,000 and about 14,500 cm^{-1} . All of the observed absorption bands can be theoretically

assigned to tetrahedral CoCl_4^- . Without additional evidence, the presence of tetrahedral CoCl_4^- in acetamidinium tetrachlorocobaltate is strongly favored.

Again, the infrared spectrum indicates that the acetamidinium cation is present in the chlorocobaltate complex.

Acetamidinium Trichloronickelate

Very little seems to be known about the NiCl_3^- species. It is interesting that the acetamidinium analogy to cesium may be extended to this case also. The crystal structure of CsNiCl_3 has been alluded to by Wells (40). The structure is one in which octahedral NiCl_6 groups sharing a pair of opposite faces are stacked in columns.

Acetamidinium trichloronickelate in ethanol shows absorption bands at 24,100 and 13,000 cm^{-1} with very low molar absorptivities of 12.3 and 4.8 respectively. A characteristic feature of octahedral Ni (II) complexes is that they possess very low molar absorptivities (41). Typical octahedral Ni (II) complexes such as $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ and $[\text{Ni}(\text{ethylenediamine})_3]^{+2}$ also have absorption bands between 11,000 and 15,000 cm^{-1} and around 25,000 cm^{-1} . If the trichloronickelate is present in solution as NiCl_3^- and not as a complex mixture of $[\text{NiCl}_n\text{L}_{3-n}]^{n-2}$, the solution spectrum strongly suggests that the complex is octahedral.

Copper (II) Acetamidinate and Copper (II) Benzamidinate

The elemental analyses on both these complexes indicate a single molecule of solvation. This is the correct stoichiometry for a dimeric syn-syn bidentate structure. Unfortunately, the complexes are so insoluble in most common solvents that the molecular weights could not be determined.

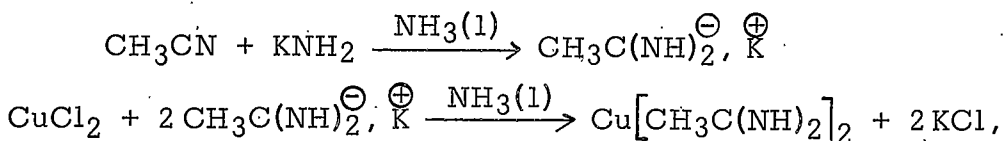
The crystal and solution spectra of the two complexes indicate that they have very similar structures. Bands around 580 $m\mu$ are not observed in the spectra of the Cu (II) carboxylates; however, 1,3-Diphenyltriazenido-copper (II), presumed to have a syn-syn bidentate structure, does absorb near 600 $m\mu$ (13). On the other hand, Gould and Jameson (42) report absorption bands at about 580 $m\mu$ for three α -hydroxyamidine complexes with copper (II). They propose for these complexes a structure in which the α -hydroxyamidine ligand acts as a chelate group, coordinating with the copper through one nitrogen and the hydroxy oxygen. Two of their reported complexes are dihydrated, the other being anhydrous.

If one plots the magnetic susceptibilities versus temperature for each of the amidinate complexes, reasonable parabolas may be drawn through the three points in each case. The susceptibilities appear to conform to the Curie-Weiss Law in the 80-298°K temperature range. Susceptibilities at a few intermediate temperatures would confirm this. Weiss constants of about +1° and -20° are obtained for the acetamidinate and benzamidinate respectively, implying that the complexes are not antiferromagnetic. Quite normal, temperature-independent magnetic moments were determined for both complexes, suggesting that the complexes are magnetically dilute.

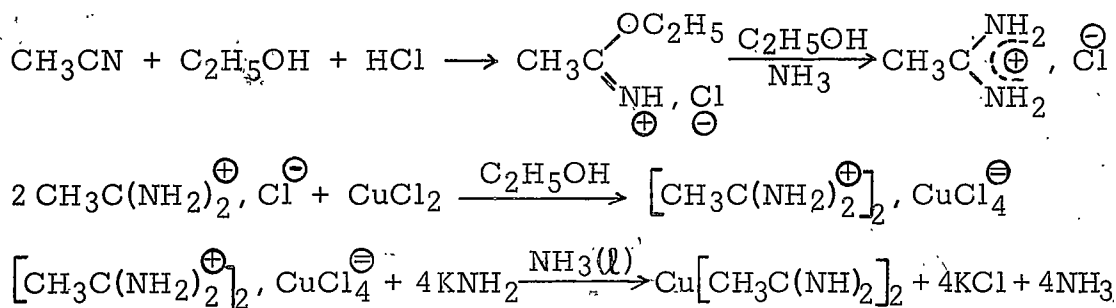
On the basis of the experimental data determined at the time of this writing, little more can be said about these complexes. Initial studies seem to hint that copper (II) acetamidinate and copper (II) benzamidinate may not be dimeric. However, until a molecular weight (or crystallographic) determination is made, one cannot be certain of this.

SUMMARY

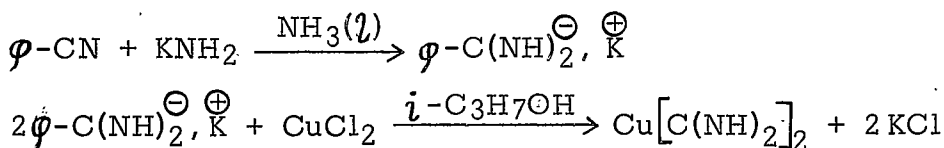
Copper (II) acetamidinate is much more difficult to synthesize than initially anticipated. The most feasible and direct approach,



failed to produce the desired product. While investigating other possible approaches, three new complexes, acetamidinium tetrachlorocuprate, acetamidinium tetrachlorocobaltate and acetamidinium trichloronickelate were prepared. One of these complexes, the cuprate, was used as an intermediate in the successful synthesis of copper (II) acetamidinate. The general synthesis of the latter is as follows:



Copper (II) benzamidinate has been prepared by the direct method,



Ultraviolet and visible solution spectra and diffuse reflectance spectra have been reported for all five of these new complexes. Magnetic susceptibilities at 80°, 196° and 298°K have been determined and reported for acetamidinium tetrachlorocuprate, copper (II) acetamidinate and copper (II) benzamidinate.

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