The Preparation of Strictly Halide Complexes of Copper(II) and Their EPR Spectra

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Copper(II) complexes are probably some of the most thoroughly studied of all the metal complexes, and many new findings in the field of EPR study have recently been obtained with these complexes. However, most of the copper complexes so far studied have been those in which ligands are coordinated through oxygen or nitrogen atoms; structurally they form elongated octahedra, with two atoms in the trans positions somewhat far from the central copper ion.

On the other hand, very little information has been obtained with copper complexes in which all the ligands are coordinated through halogen atoms. Bailar and Busch term such a compound "a strictly halide complex";[1] it is indeed in these compounds that various anomalies, both in structure and in spectra, are observed. Thus, in Cs_2CuCl_4 and Cs_2CuBr_4, tetrahalogenocuprate(II) anions form distorted tetrahedra,[2] while in $[Cr(NH_3)_6][CuCl_5]$, pentachlorocuprate(II) anion forms a trigonal bipyramid.[3] Brown compounds, $CsCuCl_3$[4] and $KCuCl_3$[5] of a polymer structure with Cl–Cu–Cl–Cu chains or the like, and a series of mixed valence compounds, $[Cr(NH_3)_6]CuCl_{5-x}$ or $[Cr(NH_3)_6]_4Cu_5Cl_{17+x}$,[6] also belong to this category. Research into these anomalous chlorocuprates seems to be necessary for a more complete understanding of the coordinate linkage in copper complexes.

As a means of studying this subject, the present authors chose to examine electron paramagnetic resonance, since it usually affords useful information, especially in connection with the state of the d electrons, electron delocalization, exchange interaction, and other problems. In particular, the accumulation of such fundamental EPR data as the *g*-values for pure copper halogen linkages can be made possible only by the use of these strictly halide complexes as specimens.

Experimental

Samples.—The chlorocuprates studied in the present research are: (1) hexamminecobalt(III) pentachlorocuprate(II), (2) hexamminecobalt(III) chlorocuprates(I, II), (3) chlorocuprates(II) of chain organic polyamines, (4) chlorocuprate(I, II) and chlorocuprate(I) of a chain organic polyamine, and (5) chlorocuprates(II) of *s*-triazine derivatives. The preparation of 1 and 2 has been described in

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[1] J. C. Bailer, Jr., and D. H. Busch, "Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York (1956), p. 5.

[2] L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

[3] M. Mori, Y. Saito and T. Watanabe, This Bulletin, **34**, 295 (1961).

[4] A. F. Wells, *J. Chem. Soc.*, **1947**, 1662.

[5] R. D. Willett, C. Dwiggins, Jr., R. F. Kruh and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).

[6] M. Mori, This Bulletin, **33**, 985 (1960). The series of chlorocuprates(I, II) reported on in this literature may be expressible by either of the above formulae. The former expresses compounnds with a ratio of copper(I) and copper(II) smaller than 1:1 and in which x is, therefore, smaller than 0.5. The latter expresses compounds with a low copper(II) content and in which x is, therefore, small. Compounds of the intermediate domain have not yet been thoroughly analyzed to afford an appropriate formula by which they can be expressed.

a previous paper.[6] Most of the compounds of group 3 are those reported by Jonassen et al.[7] In this section the procedure for preparing compounds of groups 4 and 5 will be described.

Diethylenetriammonium Chlorocuprate(I, II).— A cooled mixture of 2.5 g. of diethylenetriamine and 3 ml. of water is slowly acidified with 10 ml. of 12 N hydrochloric acid. To the mixture are added 0.5 g. of copper(I) chloride and 1 g. of copper(II) chloride dihydrate, dissolved together in a mixture of 2.5 ml. of water and 10 ml. of 12 N hydrochloric acid. When the mixture is slowly shaken 2∼3 times and allowed to stand for 1 min., small, very dark green, glistening crystals will be deposited. These are separated from the mother liquor by suction, washed with 12 N hydrochloric acid and ethanol, and dried under evacuation. Yield, 1.5 g.

Rubbing the sides of the glassware during the crystallization or allowing the mixture to stand for too long a period should be avoided, as this will cause a crystallization of a colorless copper(I) compound which is very difficult to remove from the substance to be prepared. Once colorless crystals are deposited, preparation should be repeated anew.

Found: Cu, 18.20; Cu(II), 17.85; Cl, 50.77; N, 12.16. Calcd. for $(H_3N\cdot C_2H_4\cdot NH_2\cdot C_2H_4\cdot NH_3)CuCl_{5-x}$, ($x$=0, i. e., for a divalent compound for simplicity's sake): Cu, 18.31; Cl ,51.09; N, 12.11%.

When the analytical value is considered, the copper(I) content is seen to be quite low. Nevertheless, the color (very dark green) is quite different from the yellow color of a pure copper(II) compound; moreover, the copper(II) content and the color are changed when the ratio of mixing in the preparation is changed. Thus, for example, if 0.2 g. of copper(I) chloride is used instead of 0.5 g. in the above procedure, the color of the product is more yellowish but still far deeper than the color of the pure copper(II) compound, while the composition is now almost identical with that of the copper(II) compound. An increase in the quantity of copper(I) chloride used also seems to bring about a color change, but in this case preparation becomes more difficult owing to the readiness with which a colorless copper(I) compound separates out.

Diethylenetriammonium Pentachlorodicuprate(I). The procedure is similar to that for chlorocuprate-(I, II), but 2 g. of copper(I) chloride should be used instead of a mixture of copper(1) chloride and copper(II) chloride. It forms colorless, scaly crystals.

Found: Cu, 30.76; Cl, 43.52; N, 10.64. Calcd. for $(H_3N\cdot C_2H_4\cdot NH_2\cdot C_2H_4\cdot NH_3)Cu_2Cl_5$: Cu, 30.95; Cl, 43.18; N, 10.23%.

Ethylenediammonium Tetrachlorocuprate(II), Diethylenetriammonium Pentachlorocuprate(II) and Triethylenetetrammonium Hexachlorocuprate(II).—These compounds were first reported by Jonassen et al.[7] The present research has revealed, however, that they can be much more easily prepared. For example, diethylenetriammonium pentachlorocuprate(II) can be prepared by a procedure similar to that used in preparing the chlorocuprate-(I, II) described above, except that copper(II) dihydrate is used instead of a mixture of copper(I) chloride and copper(II) chloride. The other cases are analogous.

Chlorocuprates(II) of *s*-Triazine Derivatives.— (*a*) *Dimelammonium Hexachlorocuprate(II)*. — One and three-tenths grams of melamine is dissolved as quickly as possible in 20 ml. of boiling 6 N hydrochloric acid. To this solution is added, without delay, 1.7 g. of copper(II) chloride dihydrate dissolved in 10 ml. of 6 N hydrochloric acid; the mixture is then allowed to cool for several minutes. The yellow crystals that form are collected on a glass filter and washed with 6 N hydrochloric acid and with acetone; after being dried by strong suction, they are immediately sealed in a dry glass tube.

Found: Cu, 11.72; Cl, 39.85; N, 31.62. Calcd. for $\{C_3N_3(NH_2)_3H_2\}_2CuCl_6$: Cu, 11.93; Cl, 39.95; N, 31.56%.

(*b*) *Melammonium Hexachlorodicuprate(II)*.—One gram of melamine is dissolved in 10 ml. of boiling 6 N hydrochloric acid as quickly as possible, and the solution is mixed with 3 g. of copper(II) chloride dihydrate which has previously been dissolved in 20 ml. of 12 N hydrochloric acid. The brown needles thus formed are filtered, washed with 12 N hydrochloric acid and acetone, and kept in a desiccator.

Found: Cu, 26.44; Cl, 44.84; N, 18.21. Calcd. for $\{C_3N_3(NH_2)_3H_2\}Cu_2Cl_6$: Cu, 27.15; Cl, 45.47; N, 17.96%.

(*c*) *Benzoguanammonium Trichlorocuprate(II)*. — Two grams of benzoguanamine are dissolved in 30 ml. of hot glacial acetic acid. Two grams of copper(II) chloride dihydrate dissolved in 5 ml. of 6 N hydrochloric acid are then added, and the yellowish brown needles which precipitate out are washed on a glass filter with a mixture of glacial acetic acid and ether, and dried at about 100°C. Yield, 3.0 g.

Found: Cu, 18.57; Cl, 28.57. Calcd. for $\{C_6H_5\cdot C_3N_3(NH_2)_2H\}CuCl_3$: Cu, 17.74; Cl, 29.70.

The somewhat poorer agreement in the analytical value is probably due to a contamination of the free benzoguanamine or copper(II) chloride; the contaminating to materials are difficult to remove because of their low solubility in a mixture of glacial acetic acid and ether. Washing with such other liquids as hydrochloric acid brings about a decomposition of the preparation.

The Apparatus of EPR Measurement. — The apparatus used in EPR measurements has the same features as a spectroscope working at any other wavelength. The essential components are a source of radiation, an absorption cell, and a detector. In the microwave region the source of radiation is provided by a klystron tube which can be highly stabilized to give a very monochromatic radiation. The absorption cell is a resonant cavity tuned to the klystron frequency, and the specimen can be placed in a region of high r. f. magnetic field strength. The output from the cavity absorption cell is fed to a silicon-tungsten crystal, which detects the microwave radiation and feeds its modulated

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[7] H. B. Jonassen, T. B. Crumpler and T. D. O'Brien, *J. Am. Chem. Soc.*, 67, 1709 (1945).

envelope on to amplifiers. The resonance condition is

$$h\nu = g\beta H$$

where ν is the microwave frequency; β, the Bohr magneton, and H, the applied magnetic field, and where g is termed the spectroscopic splitting factor and has a value depending on the electronic state of the atom. In the present study, EPR spetra of chlorocomplexes of copper were taken at 9375 Mc., requiring magnetic fields in the 2700∼3500 of range. The apparatus used in this experiment is one of Japan Electron Optics Company, of the JES-118, type, using an X-band generated by a Varian X-13 klystron tube. The magnetic field is modulated at 80 c. p. s. The field strength was calibrated by taking the spectra of the DPPH powder of an aqueous solution of manganese(II) sulfate.

The EPR spectra of powdered samples of chlorocuprates are shown in Fig. 1 (a)—(j). In Figs. (a) to (h), the upper curves are the derivatives of the absorption lines observed, and the lower curves, the integrated absorption lines. With the records of (i) and (j), integration could not be performed because of the extreme broadness of the absorption lines.

Results and Discussion

The Composition and the Color of the Chlorocuprates.—All strictly chloride complexes of copper(II) with an atomic ratio of chlorine to copper greater than 4 : 1 are yellow. This is probably due to the fact that the LF bands which impart blue or green colors to aquo or ammine complexes lie in the infrared region in chlorocuprates, while charge transfer bands come into the visible region in chloro complexes and give these compounds their yellowish color.

There is a group of chlorocuprates with the chlorine to copper ratio of 3 : 1. They are crystallized from solutions of high copper(II) concentration or from media of relatively concentrated acetic acid, and they are usually brown in color. Well-known examples are potassium copper(II) trichloride and cesium copper(II) trichloride, both of which have been found to be kinds of coordination polymers.[4,5] Additional examples found in the present research are melammonium hexachlorodicuprate(II) and benzoguanammonium trichlorocuprate(II), although their crystal structures are not yet known. All these compounds show characteristic EPR spectra, as will be discussed later.

The dark green color of diethylenetriammonium chlorocuprate(I, II) is probably due to the interaction of univalent and divalent copper ions.

EPR Absorption Spectra.—Most of the EPR data presented here are those of powdered samples. Kneubühl[8] developed a method to get EPR data from the spectra of powdered samples and applied it to the interpretation of the spectra of anisotropic copper ions. The method seems particularly convenient for the comparison of the EPR spectra of more or less analogous componuds.

Among the chlorocuprates studied in the present research, dimelammonium hexachlorocuprate(II) was the only compound that showed the fine structure of an anisotropic g-tensor. (Fig. 1(h)). By means of the method described by Kneubühl, the components of the g-tensor were evaluated as $g_{//}=2.32$ and $g_{\perp}=2.08$ for this compound.

All the other chlorocuprates studied showed single lines with half-widths ranging from 110 to 220 oe. Generally speaking, a single line can be observed either when three components of a g-tensor coincide with each other or when the superexchange interaction is great enough to smear out the effect of crystal anisotropy. The former can hardly be the case for Cu^{2+} ions in solid samples, as has in many cases been confirmed experimentally and theoretically.[9] The appearance of single lines in some copper compounds is, therefore, to be explained in terms of the latter effect.[10] In order to smear out the fine structure with the components of the g-tensor ranging from 2.08 to 2.32, the interaction energy corresponding to the exchange should be about $10^9\,\text{sec}^{-1}$. The fact that only dimelammonium hexachlorocuprate showed the superfine structure of an anisotropic g-tensor may be due to the screening effect of large planar organic molecules present in the crystal lattices of this compound.

There are two ways in which the superexchange of paramagnetic ions influence the line width of the EPR spectra: one is to broaden the width, and the other is to reduce it. The former effect, termed exchange broadening, is observed in a critical case when the exchange frequency is nearly equal to the energy separation between the resonance points divided by Planck's constant. The EPR spectra of the chlorocuprates of chain organic polyamines seem to exemplify such a case; the half width is about 200 oe, and the shape of the curve is of a bell type, with an assymmetric contour (Figs. 1 (d)—(f)).

The latter case (exchange narrowing) is the one in which the exchange frequency is greater than that in the critical case above mentioned; it is characterized by a line shape of the Lorenzian type. The EPR spectra of hexamminecobalt(III), pentachlorocuprate(II) and related

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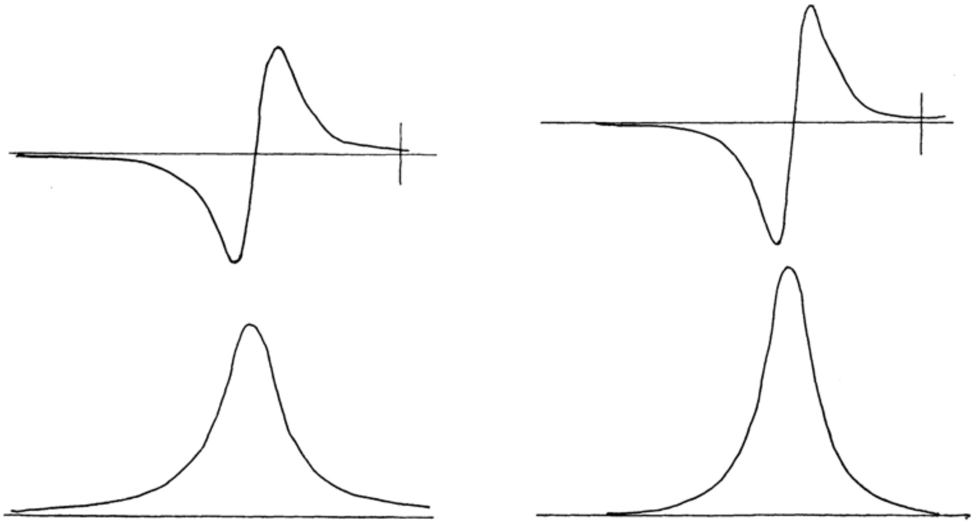
[8] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[9] L. E. Orgel and J. D. Dunitz, *Nature*, **179**, 462 (1957).

[10] D. M. S. Bagguley and J. H. E. Griffiths, *Proc. Roy. Soc.*, **A201**, 366 (1950).

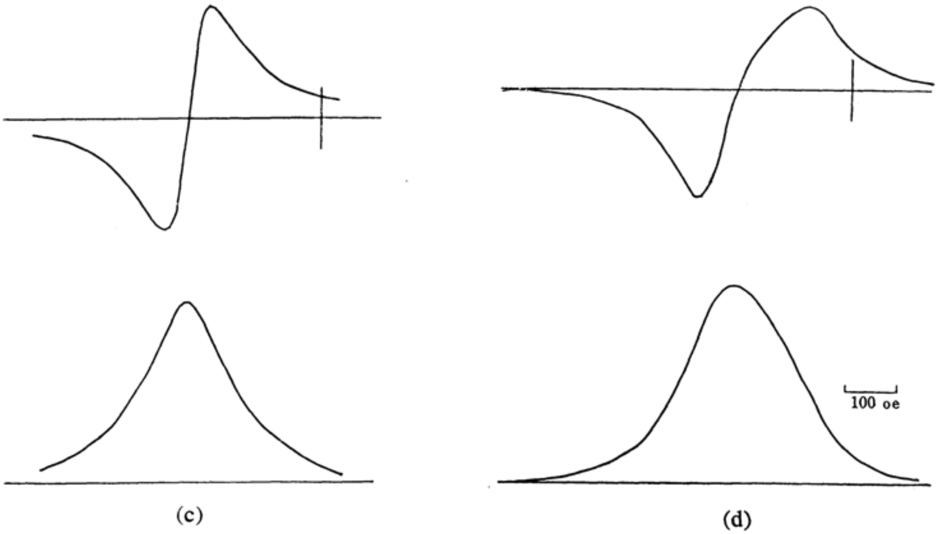
TABLE I. THE EPR DATA OF CHLOROCUPRATES

Compound	g.	ΔH_{msl}	$\Delta H_{1/2}$	$\Delta H_{1/2}/\Delta H_{\mathrm{msl}}$	$\sqrt{\overline{\Delta H^2}}$	$\mathrm{Cu^{II}/Cu}\times 100$
$[\mathrm{Co(NH_3)_6}]\mathrm{CuCl_5}$	2.17	86	140	1.63		100
$[\mathrm{Co(NH_3)_6}]\mathrm{CuCl_{5-x}}$	2.16	64	105	1.64	80	78
$[\mathrm{Co(NH_3)_6}]_4\mathrm{Cu_5Cl_{17+x}}$	2.17	68	116	1.70	90	10
$[\mathrm{Co(NH_3)_6}]_4\mathrm{Cu_5Cl_{17+x}}$	2.17	88	183	2.10		
$\mathrm{dienH_3CuCl_{5-x}}$	2.14	162	218	1.35		98
$\mathrm{enH_2CuCl_4}$	2.14	148	222	1.50		100
$\mathrm{dienH_3CuCl_5}$	2.14	139	185	1.33	108	100
$\mathrm{trienH_4CuCl_6}$	2.14	139	218	1.57		100
$\mathrm{(melamine)_2H_4CuCl_6}$	2.31 2.08					100



(a) $[\mathrm{Co(NH_3)_6}][\mathrm{CuCl_5}]$

(b) $[\mathrm{Co(NH_3)_6}][\mathrm{CuCl_{4.74}}]$

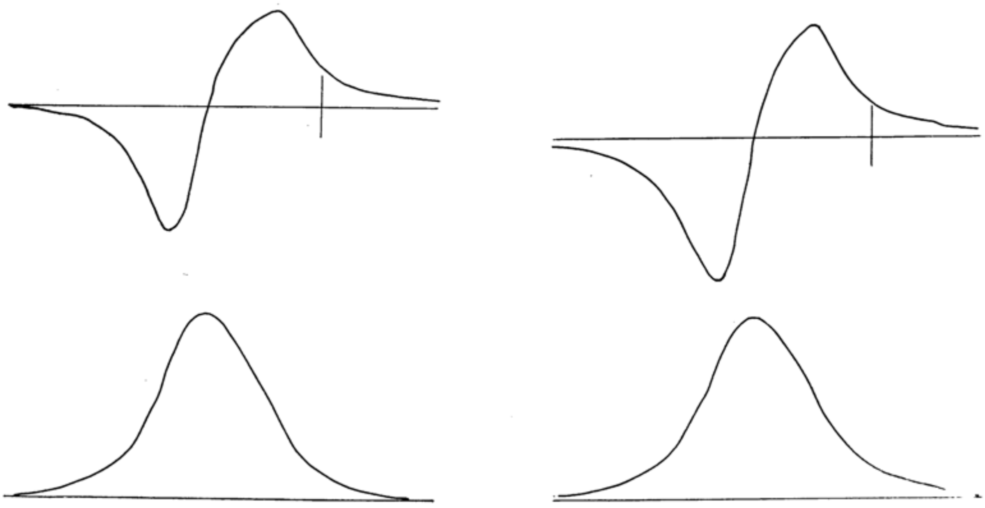


(c) $[\mathrm{Co(NH_3)_6}]_4\mathrm{Cu_5Cl_{17+x}}$

(d) $\mathrm{enH_2CuCl_4}$

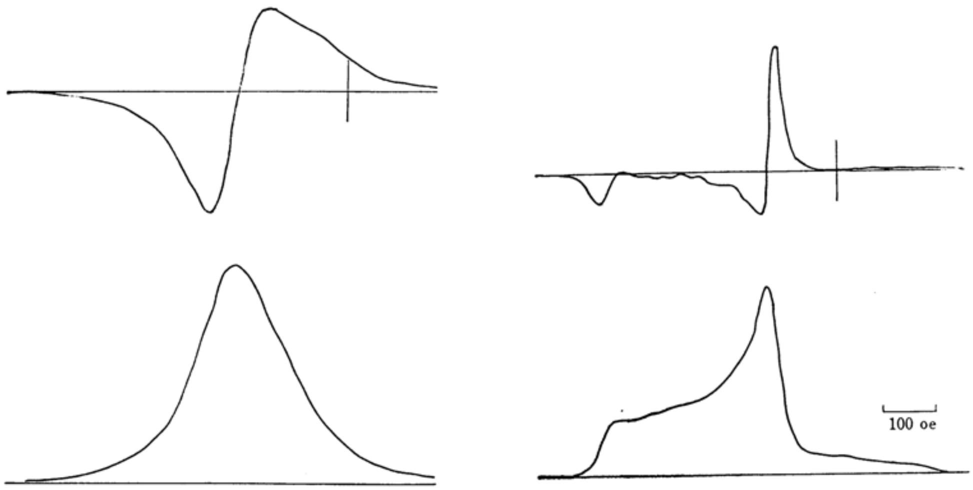
Fig. 1. EPR spectra of chlorocuprates.

The short vertical line on the right hand side of each derivative curve is the marker of the maximum point of a DPPH absorption line.



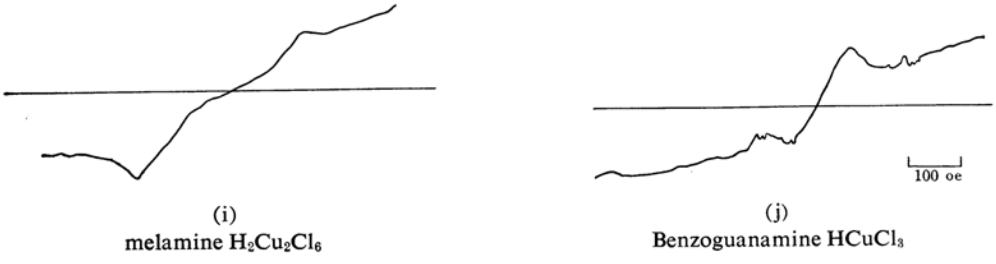
(e)
dien H_3CuCl_5

(f)
trien H_4CuCl_6



(g)
dien $H_3CuCl_{4.98}$

(h)
(melamine)$_2H_4CuCl_6$



(i)
melamine $H_2Cu_2Cl_6$

(j)
Benzoguanamine $HCuCl_3$

Fig. 1. continued.

mixed valence chlorocuprates(I, II) seem to fall in this category, since the lines are comparatively narrow (80 oe) and the ratio of the line width at the half-maximum point, $\Delta H_{1/2}$, to that at the points of maximum slopes, ΔH_{msl}, is about 1.7. The symmetric line shape of the EPR absorption spectra may be taken as partly due to the special character of the $CuCl_5^{3-}$ ion, with all the Cu–Cl distance almost identical to one another.[3] Even the line shape of the spectra of a single crystal showed scarcely any angular dependence on the field directions.

The width of the curve is narrower in the chlorocuprates(I, II) than in chlorocuprate(II) in this series when the content of copper(I) is not high. It seems, however, difficult to decide whether this is due to the effect of the dilution of copper(II) or to enhanced exchange interaction caused by the presence of copper(I). When the content of copper(I) becomes overwhelmingly higher than that of copper(II), the width again increases; this is probably due to the increased field anisotropy. The main EPR data of chlorocuprates of various compositions are presented in Table I.

As has been pointed out at the beginning of this discussion, chlorocuprates with a chlorine to copper ratio of 3 : 1 have a brown color and are considered to have polynuclear structures. The EPR spectra of such compounds have invariably a very broad line width to cover thousands of oersteds, and the *g*-values of these lines can be evaluated only with difficulty (Figs. 1 (i) and (j)). This broadening can perhaps be attributed to the strong exchange and dipolar action and to the great anisotropy of the crystal field, both arising from the linear structure in the crystal lattices.

Summary

Some copper complexes which have only chloride ions in the coordination spheres have been prepared and their EPR spectra examined at the microwave frequency of the X-band. Most of these compounds gave single EPR lines with half-widths ranging from 110 to 220 oe; this seems to indicate the existence of superexchange interaction. Only the yellow plates of dimelammonium hexachlorocuprate(II) showed the fine structure of an anisotropic *g*-tensor, from which fact the *g*-components were evaluated as $g_{\parallel}=2.32$ and $g_{\perp}=2.08$ for this compound. The dark green color of diethylenetriammonium chlorocuprate(I, II) is probably due to the interaction of Cu^+ and Cu^{2+} in the crystal lattices. Brown chlorocuprates with a chlorine to copper ratio of 3 : 1 are probably coordination polymers; the EPR lines of these compounds are so broad as to cover thousands of oersteds.

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