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CHLOROCUPRATES(II)

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CONTENTS

A. INTRODUCTION

This review deals with copper(II) compounds $A_xCu_yCl_z$, where A is a discrete cation. We are concerned exclusively with $CuCl_n$ chromophores; most hydrated chlorocuprates(II) fall outside our scope, since they usually contain coordinated water molecules. However, we shall discuss selected work on such compounds if it is relevant to the Cu—Cl bonding in chlorocuprates(II). We shall also discuss appropriate aspects of $CuCl_2$ and $CuCl_2 \cdot 2H_2O$. Emphasis is placed on the physical properties of chlorocuprates(II) in relation to their structures.

Some previous reviews have covered the subject of chlorocuprates(II) within a broader chemical context. Hatfield and Whyman [1] have reviewed copper complexes in general, up to 1968. A comprehensive list of references on derivatives of $CuCl_2$ (though with limited discussion) up to about 1968 is found in the valuable monograph of Colton and Canterford [2]; Colton [3] has extended coverage through 1971. Some other reviews dealing with, for example, specific physical properties will be mentioned in the appropriate places later.

In Sect. B, we discuss general features of chlorocuprates(II), including preparation, stoichiometry and the stabilizing cations. Section C describes the structures of crystalline chlorocuprates(II), as determined by X-ray crystallography. The large subject of electronic spectra is conveniently divided into two parts, ligand field spectra in Sect. D and charge transfer spectra in Sect. E. Section F covers the vibrational spectra of chlorocuprates(II), and Sect. G describes their magnetic and ESR properties. Section H discusses miscellaneous physical measurements, and in Sect. I we discuss briefly such aspects of chlorocuprates(II) in solution as are relevant to the situation in crystalline chlorocuprates(II). We have attempted to cover the literature from 1964 to 1975, with more selective coverage of earlier work.

B. GENERAL FEATURES

Here we survey the stoichiometries of chlorocuprates(II), preparative routes, the counter-cations found, and some practical applications.

(i) Some problems of nomenclature and notation

The conventional scheme for the nomenclature and notation of coordination compounds is not wholly satisfactory for copper(II) species. The scheme emphasises the importance of specifying which groups are coordinated to the metal and which are not, but this is not always clear with copper(II) in a highly distorted environment, even after a complete X-ray analysis has been performed. For example, in $Cu(NH_3)_4X_2$ the X groups form long bonds to the metal and have been described as 'semi-coordinated' [4—6]. It is arguable whether we should write $[Cu(NH_3)_4X_2]$ or $[Cu(NH_3)_4]X_2$, and whether we should name the compound as a molecular complex or as a complex salt.

Even worse problems confront us in dealing with chlorocuprates(II). As we shall see in Sect. C, their structural diversity requires a full structure determination before we can begin to give them systematic names. For example, the compounds previously known as tris(dimethylammonium) pentachlorocuprate(II) $[(CH_3)_2NH_2]_3[CuCl_5]$ and bis(2-ammonioethyl)ammonium pentachlorocuprate(II) $[(NH_3CH_2CH_2)_2NH_2][CuCl_5]$ are now referred to as tris(dimethylammonium) tetrachlorocuprate(II) monochloride and bis(2-ammonioethyl)ammonium tetrachlorocuprate(II) monochloride, following X-ray analyses which reveal one lattice chloride ion per formula unit; but these names and formulae fail to convey the fact that the coordination about the metal is drastically different in the two compounds. The former contains discrete tetrachlorocuprate(II) ions, but the latter does not; the former has four-coordinate copper, but in the latter the metal has tetragonal octahedral six-coordination (or 4 + 2 coordination).

For the purpose of classification meanwhile, we shall adopt a nomenclature scheme based simply on stoichiometry. Thus we shall refer to potassium trichlorocuprate(II) $KCuCl_3$, rather than to dipotassium di-μ-chlorotetrachlorodicuprate(II) $K_2[Cu_2Cl_6]$. We shall use square brackets to indicate discrete entities only in the case of cations. This will avoid difficulties in dealing with chlorocuprates(II) of unknown or uncertain structure, as well as inconsistencies and doubts with respect to distant 'semi-coordinated' groups. Thus the two compounds cited in the previous paragraph will both be classified as pentachlorocuprates(II), without any implication that they contain discrete $[CuCl_5]^{3-}$ ions.

(ii) Stoichiometry

The known stoichiometries of chemically-characterised chlorocuprates(II) are summarised in Table 1. The most common and familiar are the trichloro-

TABLE 1

Stoichiometries of known chlorocuprates(II) (A signifies a cation, and the number of primes its charge)

$A'CuCl_3$	$A''CuCl_4$	$A'''CuCl_5$	$A''''CuCl_6$
$(A')_2CuCl_4$	$A''Cu_2Cl_6$		
$(A')_3CuCl_5$			
$(A')_4CuCl_6$			
$A'Cu_2Cl_5$			
$(A')_3Cu_2Cl_7$			
$(A')_5Cu_3Cl_{11}$			

cuprates(II) $A'CuCl_3$ and tetrachlorocuprates $(A')_2CuCl_4$. Some compounds have been referred to as pentachlorocuprates(II) without firm evidence that they are not merely mixtures of $(A')_2CuCl_4$ and $A'Cl$. Few hexachlorocuprates(II) have been reported [7—9] and little is known about them.

(iii) Cations found in chlorocuprates(II)

A remarkable variety of cations serve as counter-ions in chlorocuprates(II), ranging from simple alkali metal cations to highly complex organic, inorganic and even organometallic species. References are given here only to work on chlorocuprates(II) whose very existence is of interest; the more familiar chlorocuprates(II) will be covered at length in following sections.

(a) Simple inorganic cations

Amongst the alkali metals, the best-known chlorocuprates(II) are $KCuCl_3$, $CsCuCl_3$ and Cs_2CuCl_4. Others which have been reported include Li_2CuCl_4, K_2CuCl_4, Rb_2CuCl_4 and Cs_3CuCl_5. The catalytic activity of Li_2CuCl_4 will be discussed below, but little is known about this material. K_2CuCl_4 remains an enigma. Its melting point [10] and heat of formation [11] have been reported, and it is said [12,13] to be isostructural with Cs_2CuCl_4. However, a recent investigation [14] suggests that anhydrous K_2CuCl_4 does not exist; attempts to prepare it always give a mixture of $KCuCl_3$ and KCl. The dihydrate decomposes on heating above 93° to KCl, $KCuCl_3$ and water [15,16]. However, the most recent work [17] reports the successful dehydration of $K_2CuCl_4 \cdot 2H_2O$ to K_2CuCl_4. The phase diagram for the system $KCl/CuCl_2$ shows $KCuCl_3$ as a congruently-melting compound, but not K_2CuCl_4 [18]. Rb_2CuCl_4 is a well-defined compound [14]; Cs_3CuCl_5 is probably isostructural with Cs_3CoCl_5 [19].

It is a little strange that no sodium chlorocuprates(II), hydrated or not, have been reported. It cannot be argued that only the largest cations form chlorocuprates(II) since $LiCuCl_3 \cdot 2H_2O$ and Li_2CuCl_4 are known. The phase diagram for the system $NaCl/CuCl_2$ reveals no compound formation [18]. It may be significant that NaCl has the highest melting point of the alkali metal chlorides; the melting point of the eutectic mixture containing 46% $CuCl_2$ (molar) is 386°, at about which temperature $CuCl_2$ begins to decompose to CuCl and chlorine.

Other simple inorganic cations which form chlorocuprates(II) are Ag^+ and Tl^+; we may also include NH_4^+ as a simple cation. Silver forms only $AgCuCl_3$, which has been little studied [7]. Thallium(I) is reported to form Tl_4CuCl_6 and $Tl_5Cu_3Cl_{11}$ [7]; again, little else is known about these. However, NH_4CuCl_3 and $(NH_4)_2CuCl_4$ have been studied in detail, and their properties will be discussed in later sections.

The only chlorocuprate(II) of a simple dipositive cation is $FeCuCl_4$; magnetic and Mössbauer work indicate that it is indeed $Fe(II)Cu(II)Cl_4$, rather than $Fe(III)Cu(I)Cl_4$ [20].

(b) Complex inorganic cations

As discussed further below, there are many examples of chlorocuprates(II) of the type $[CuL_4]CuCl_4$, polymerisation isomers of CuL_2Cl_2 where L is a neutral base. Other interesting examples of inorganic cations stabilized in chlorocuprates(II) include $[Li(diacetamide)_2]^+$, in $[Li(diacetamide)_2]_2\,CuCl_4$ [21] and $[Mg(H_2O)_6]^{2+}$ in $[Mg(H_2O)_6]CuCl_4$ [22], although there is some doubt as to whether the coordination sphere of the copper consists exclusively of chloride ions. Another complex Mg(II) cation is found in $[MgCl(DIMP)(H_2O)_4]CuCl_3 \cdot DIMP$ (DIMP = diisopropyl methylphosphonate); the DIMP molecule outside the coordination sphere of the cation is not coordinated to the copper, according to IR studies [23].

The pentachlorocuprates(II) $[M(NH_3)_6]CuCl_5$ (M = Cr, Co, Ru, Rh, Ir) have been extensively studied, and will be discussed at length in later sections.

Some octahedral complex cations of the Group IV elements stabilize chlorocuprates(II), for example $[Si(acac)_3]CuCl_3$ [24]; complexes of the type $[MX_3]CuCl_3$ (X = imidophosphinate) are known for M = Si, Ge and Sn [25].

Phosphonitrilium derivatives form chlorocuprates(II), such as $[(NPMe_2)_5H_2]CuCl_4 \cdot H_2O$ [26]. A novel phosphorus—sulphur cation is found in $[(Me_2N)_3P{-}S{-}S{-}P(NMe_2)_3]Cu_2Cl_6$ [27]. A number of complex halides of unknown structure contain Cu(II), for example $Cs_4CuAu_2Cl_{12}$ [28].

(c) Organic cations

The most important of these are the substituted ammonium cations RNH_3^+, $R_2NH_2^+$, R_3NH^+ and R_4N^+ (R = alkyl or aryl). Many examples of alkylammonium chlorocuprates(II) will appear in subsequent sections. Multiply-charged cations derived from polyamines are also important. Quaternary phosphonium and arsonium cations are also found; $[P(CH_2Cl)_4]CuCl_3$ is a rather interesting example [29].

Many other common organic bases (e.g. pyridine derivatives) form chlorocuprates(II) such as $(LH_2)CuCl_4$. Diazonium cations ArN_2^+ are also known in chlorocuprates(II) [30—32].

A fair number of sulphur-containing organic cations form chlorocuprates-(II), including dithiolium cations in, for example, $[C_9H_7S_2]CuCl_4$ [33].

It seems that practically any stable organic cation can form a chlorocuprate-(II), as will some otherwise unstable cations; for example, $(qoH_2)CuCl_4$ (qoH = 4-chloro-2-nitrosophenol) was the first example of a salt containing a protonated benzoquinoxime cation [34]. An example of an organometallic cation is found in bis(2-pyridoyl-*N*-onium-ferrocenoyl-methano)copper(II) trichlorocuprate(II) [35].

(iv) Preparation

Most chlorocuprates(II) have been prepared by mixing solutions containing the appropriate molar ratios of $CuCl_2$ and an ionic chloride. Some chlorocuprates(II) can be crystallised from aqueous solution, including Cs_2CuCl_4, $KCuCl_3$, $CsCuCl_3$ and some alkylammonium chlorocuprates(II) [36]. Alkali metal chlorocuprates(II) can also be obtained by melting mixtures of $CuCl_2$ and MCl [7,14,37]. $[Mg(H_2O)_6]CuCl_4$ was obtained by fusing the salts together [22]. The most general preparation for chlorocuprates(II) with organic cations is by crystallisation from ethanol [38]. Other polar, weakly-coordinating solvents can be used; thionyl chloride has been recommended as a medium for the preparation of halogenometallates [39] but such rigorously anhydrous conditions do not appear to be necessary for chlorocuprates(II). In the standard preparation in ethanol, $CuCl_2 \cdot 2H_2O$ can often be used, and the ethanol need not be perfectly dry.

The deliberate preparation of a chlorocuprate(II) by these methods is rarely difficult. Of much greater interest is the unexpected preparation of a chlorocuprate(II) in a reaction from which other products were desired. The older literature contains many references to such compounds as $CuCl_2L_2 \cdot 2HCl$, where L is a neutral ligand, with the implication that L molecules are coordinated to the copper(II). These should nearly always be formulated as $(LH)_2CuCl_4$. Even in cases where the LH cation is still capable of functioning as a ligand, it may remain uncoordinated to the copper. The compound originally formulated as $CuCl_2$(thiamine) · 2HCl was believed, on the basis of IR spectra, to contain monoprotonated thiamine, bonded to the copper via a pyrimidine nitrogen atom [40]. But X-ray analysis [41] shows that the thiamine moiety is present in the lattice as a discrete, doubly-charged cation (see Sect. C).

$(Acetamidinium)_2CuCl_4$ was prepared in an attempt to obtain a copper(II)—acetamidine complex [42,43] and similar fates have befallen efforts to prepare copper(II) complexes with 3-(2-diethylamineethoxy)-1,2-benzisothiazole [44] and *N,N,N',N'*-tetraethylethylenediamine [45]. A bizarre case was the attempted preparation of a complex between $CuCl_2$ and *dl*-methamphetamine [46]; C-demethylation took place and the product turned out to be bis(*N*-methylphenethylammonium) tetrachlorocuprate(II). As noted already, the reaction between $CuCl_2$ and $(Me_2N)_3PS$ produced $[(Me_2N)_3PS{-}SP(NMe_2)_3]Cu_2Cl_6$ [27].

Other attempts to prepare CuL_2Cl_2 complexes have produced instead its polymerisation isomer $[CuL_4]CuCl_4$. In some cases, both isomers have been isolated, for example $CuCl_2(DA)_2$ and $Cu(DA)_4CuCl_4$ (DA = diacetamide) [47]. Copper(II) seems to have a greater tendency to behave in this way than other neighbouring elements in the first transition series. For example, Black [48] studied complexes of 2,2′-dipyridyl sulphone, 2,2′-dipyridyl sulphide and 2-pyridyl-2-thiazolylamine with MCl_2. Copper(II) gave invariably CuL_2-$CuCl_4$, while Co(II), Ni(II) and Zn(II) gave $MLCl_2$. Tertiary arsine oxides react with MCl_2 (M = Mn, Fe, Co, Ni, Zn) to give ML_2Cl_2 but $CuCl_2$ yields CuL_4CuCl_4 [49—51]. Slightly different examples of polymerisation isomer formation include $CuL_4 \cdot Cu_2Cl_6$ (L = tetramethylene sulphoxide) [52] and Cu(terpyridyl)Cl · $CuCl_3$ [53].

Chlorocuprates(II) can be prepared by metathetical reactions, e.g. Cu-(triptam)$_2$ · $CuCl_4$ by the reaction between Cu(triptam)$_2$(ClO_4)$_2$ and $(NEt_4)_2$-$CuCl_4$ (triptam = tris(2-pyridyl)amine [54]. A related reaction is the preparation of $(NEt_4)_5Cu_3Cl_{11}$ by the treatment of $CuCl_2$ with $[(NEt_4)]_3[VO(NCS)_5]$ in ethanol, in an attempt to prepare a complex containing V(IV) and Cu(II) bridged together [55].

Chlorocuprates(II) also result from the reaction between $CuCl_2L_2$ (L = pyridine base) and chlorine in ethanol, to give $(LH)_2CuCl_4$ [56,57]. This curious reaction presumably involves the oxidation of ethanol by chlorine to give HCl amongst other products, which reacts with the neutral complex to give the chlorocuprate(II). There are other examples of this type of reaction, for example the preparation of the protonated benzoquinoxime chlorocuprate-(II) already mentioned [34].

(v) Properties

Crystalline chlorocuprates(II) may appear in various shades of yellow, brown, red, orange or green at room temperature; many are thermochromic, as will be discussed further in Sects. C and D. Most chlorocuprates(II) with organic cations dissolve in a variety of organic solvents, usually with some solvolysis (see Sect. I), but they are decomposed by water, whose molecules invade the coordination sphere of the copper. Most chlorocuprates(II) are hygroscopic to some degree, and should be handled in dry conditions. The intricate structural, optical and magnetic properties of chlorocuprates(II) will occupy the bulk of this article.

(vi) Applications of chlorocuprates(II)

Cupric chloride has been used as a catalyst in a vast number of reactions, both in the laboratory and in the large-scale plant; a detailed account of these would justify a lengthy monograph. A venerable example is the Deacon process for the manufacture of chlorine by the oxidation of HCl; the catalyst consists of clay balls impregnated with aqueous $CuCl_2$. More recently, the role of $CuCl_2$ as a catalyst in the Wacker process [58] has attracted interest. It seems likely that in many of the catalytic functions of $CuCl_2$, a chlorocuprate(II) is actually the active species. However, many chlorocuprates(II) themselves are used as catalysts.

Li_2CuCl_4 catalyses cross-coupling reactions between Grignard reagents and alkyl bromides in tetrahydrofuran [59] and also catalyses the oxidative dimerisation of primary alkyl groups under similar conditions [60]. Bis(pyridinium) tetrachlorocuprate(II), in pyridine/HCl, catalyses the chlorination, oxychlorination, oxidation and/or oxidative dehydrogenation of ethylene, ethane and *p*-xylene [61]. Ammonium trichlorocuprate(II) catalyses the polymerisation of dimethylcyclosilazanes [62].

Benzothiazolium chlorocuprates(II) have been patented [63,64] for the control of helminths and the stimulation of animal growth, as well as for the control of aquatic crustaceans and parasites in animals.

C. X-RAY CRYSTAL STRUCTURES

Over thirty chlorocuprates(II) have been subjected to full X-ray analyses. This considerable effort has been amply rewarded by the discovery of a remarkable range of structural types. If, for the meanwhile, we classify chlorocuprates(II) according to stoichiometry, we can identify five types of trichlorocuprates(II), four of tetrachlorocuprates(II) and four of pentachlorocuprates(II), not to mention other stoichiometries. Moreover, many chlorocuprates(II) exhibit phase transitions which may be accompanied by marked structural changes, and in some cases, two distinct types of coordination geometry about the copper are found in the same phase. In this section we survey X-ray crystallographic data for chlorocuprates(II), with emphasis on the coordination geometry, interactions between recognisable chlorocuprate(II) anions in the crystal, and the role of the cation in determining the overall structure. We also discuss relevant theoretical work. It will be convenient from now onwards to classify chlorocuprates(II) according to structural types, irrespective of stoichiometry.

(i) Chlorocuprates(II) containing discrete $CuCl_4^{2-}$ ions

This category includes many tetrachlorocuprates(II) and at least one pentachlorocuprate(II). The anion is usually described as a flattened tetrahedron, of approximately D_{2d} symmetry (Fig. 1). Two Cl—Cu—Cl angles are greater than the tetrahedral angle of 109.5°, while the other four are smaller. The greater angle θ is usually taken as a measure of the distortion from T_d symmetry; in regular D_{2d} symmetry, the greater angles are equal, but in practice this is only approximately true and the mean value may be used. The square coplanar $CuCl_4^{2-}$ ion is an extreme case of a flattened tetrahedron, with two Cl—Cu—Cl angles of 180° and four of 90°. In Table 2 we list the mean Cu—Cl bond length and the mean flattening angle θ for discrete $CuCl_4^{2-}$ ions in crystals.

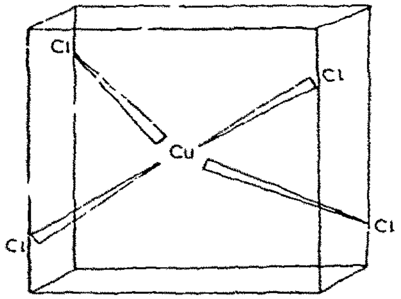

Fig. 1. Configuration of the $CuCl_4^{2-}$ ion.

TABLE 2

Structural parameters for $CuCl_4^{2-}$ ions (R is the mean Cu—Cl distance and θ is the flattening angle as defined in the text. Standard deviations are given in parentheses)

Compound	R (Å)	θ (deg)	Ref.
Cs_2CuCl_4	2.230(4)	129.2(2)	65
$(NMe_4)_2CuCl_4$	2.230(10)	129.3(3)	66
$(NEt_3H)_2CuCl_4$	2.241(2)	134.9(1)	67
$(NMe_2H_2)_3CuCl_5$ [a]	2.230(7)	135.8(2)	68
$(Me_2CHNH_3)_2CuCl_4$ [b]	2.262(9)	159.2(3)	69
	2.271(10)	151.7(3)	
$(NMe_3H)_3Cu_2Cl_7$ [c]	2.240(10)	110.6(4)	70
$(PhCH_2NMe_3)_2CuCl_4$	2.256(3)	132.5(2)	71
$(PhCH_2CH_2NMeH_2)_2CuCl_4$	2.209(4) [d]	130.6(2) [d]	46
	2.265(1) [e]	180.0(1) [e]	
$(PhCH_2CHMeNMeH_2)_2CuCl_4$ [f]	2.236(6)	139.2(3)	72
	2.241(6)	137.3(3)	
$(C_{12}H_{18}N_4OS)CuCl_4$	2.254(3)	133.8(1)	41
$[Pt(en)_2Cl_2]CuCl_4 \cdot H_2O$	2.258(5)	154.1(2)	73
$(pq)CuCl_4$ [g]	2.247(1)	129.2(1)	74
$[(NPMe_2)_5H_2]CuCl_4 \cdot H_2O$	2.255(3)	133.5(1)	26
$(C_{13}H_{19}N_2OS)_2CuCl_4$	2.240(3)	143.5(1)	44
$(PPh_4)_2CuCl_4 \cdot H_2O$	2.243(2)	128.7(1)	75

[a] One Cl^- per formula unit is uncoordinated.

[b] Four crystallographically distinct Cu atoms are found in the unit cell. A fifth Cl atom is found at 3.12(2) and 3.33(1) Å along the (approximately) S_4 axes of the respective Cu atoms whose coordination geometries are described in the table.

[c] This compound contains two crystallographically distinct Cu atoms.

[d] High-temperature form.

[e] Low-temperature form.

[f] This compound contains two types of $CuCl_4^{2-}$ ions.

[g] pq = $[N,N'\text{-dimethyl-4,4'-bipyridinium}]^{2+}$.

The configuration of the tetrachlorocuprate(II) ion has aroused great interest since it was first reported in Cs_2CuCl_4 in 1952 [76]. The Jahn—Teller theorem predicts that the $^2T_2$ ground state of a tetrahedral d^9 ion should be unstable with respect to distortion, and it can be further argued on qualitative grounds [77] that a flattening towards D_{2d} symmetry is likely. However, it has been pointed out [78] that spin-orbit coupling will lift the degeneracy of the tetrahedral ground state and it is not clear whether the magnitude of the spin-orbit splitting is sufficient to satisfy the Jahn—Teller theorem. Dunn has argued [79] that no Jahn—Teller-active mode of vibration can perform the required distortion in $CuCl_4^{2-}$, and the significance of the Jahn—Teller theorem was called further into question with the first reported X-ray analysis of a tetrachloronickelate(II) [80] in which the predicted Jahn—Teller distortion failed to appear. The fact that $CoCl_4^{2-}$ and $ZnCl_4^{2-}$ ions sometimes exhibit significant flattening towards D_{2d} symmetry [81—84] suggests that crystal forces might be important in determining the geometries of tetrahalogeno-ions. How far, then, is the configuration of the $CuCl_4^{2-}$ ion an intrinsic property, and how far may it be influenced by crystal forces?

An obvious approach might be to calculate the energy of the ion as a function of the flattening angle θ, and see whether a minimum can be found. Such a calculation was attempted as early as 1956 by Felsenfeld [85], using an ionic model with allowance for polarization of the ions. It was found that the electronic energy of the ion was lowered by flattening from T_d towards D_{4h}, while the repulsion between Cl^- ions increased. A balance between these two factors was struck at an angle θ of 123°, close to the experimental value. Unfortunately, the *d—d* spectrum of $CuCl_4^{2-}$ had not been properly analysed at the time and Felsenfeld calculated the required crystal field parameters using Slater-type 3*d* functions; these splitting parameters are far removed from those subsequently found experimentally (see Sect. D). Semi-empirical MO calculations [86—88] have likewise found an energy minimum for $\theta \sim 120°$; in these, the balance is between the energies of the bonding and antibonding MO's, and the repulsion between chloride ions is not explicitly considered. The most elaborate analysis [89] involves the calculation of the total energy of the ion, using ab initio methods, for a range of θ values; again, an energy minimum was found near 120°. It is remarkable that these very different theoretical models all reach much the same conclusion, namely that the distortion in $CuCl_4^{2-}$ is an intrinsic property of the isolated ion.

An alternative approach is an experimental one; the effects of crystal forces on the configuration of the anion might be distinguished from any intrinsic propensity towards distortion by measuring physical properties which are sensitive to the coordination geometry in a variety of crystalline and non-crystalline environments. Sharnoff [90,91] measured the ESR spectrum of $CuCl_4^{2-}$ doped in Cs_2ZnCl_4 and obtained different *g*-values from those in Cs_2CuCl_4. Subsequent work [92] showed that, although lattice effects did change the ESR spectrum, they were so small that an intrinsic distortion of the anion had to be postulated. Various physical measurements on the

$CuCl_4^{2-}$ ion in non-coordinating solvents [93,94] suggest that its configuration is much the same as in the crystalline state.

It has recently become possible to calculate directly the effects of crystal forces on ions [65,95,96]. McGinnety [65] has performed a detailed analysis for Cs_2CuCl_4. The electrostatic field of the cations causes compression of the Cu—Cl bonds in the anion, and McGinnety concludes that the Cu—Cl distance in an isolated $CuCl_4^{2-}$ ion would be 2.270 Å, or 2.283 Å after corrections for thermal motion. This work was mainly concerned with the effects of crystal forces upon bond lengths rather than bond angles, and the question of the configuration of the $CuCl_4^{2-}$ is not completely cleared up. However, the self-consistency of McGinnety's calculations is impressive and we feel compelled to accept his description of the isolated $CuCl_4^{2-}$ ion as being flattened with $\theta \sim 129°$.

With more complex cations than Cs^+ we may have to consider the effects of hydrogen bonding. If, for example, there is appreciable NH···Cl interaction the fractional charge on the Cl atom will be reduced and the crystal forces acting upon it will be diminished, leading to elongation of the Cu—Cl bond. We may also expect the Cl—Cu—Cl angles to be affected, if we think in terms of Felsenfeld's simple model where the configuration of the anion arises from a balance struck between the electronic requirements of the metal and the repulsive forces between ligands. This leads us to a more detailed discussion of the data in Table 2. How far can we rationalise the variations in bond lengths and angles? We might predict a correlation between the mean Cu—Cl distance and the flattening angle θ, with the longest bonds in the flattest tetrahedra. An inspection of the data shows that the four longest Cu—Cl bonds are indeed associated with the flattest tetrahedra but the correlation is, on the whole, rather poor. This suggests that the additional repulsion arising from closer approach of the ligands to one another as the tetrahedron is flattened is somehow reduced or compensated. Hydrogen bonding must therefore be explicitly considered. It may be noted that in the four compounds in Table 2 where no hydrogen bonding is likely (there being no polar X—H bonds in the cation) the flattening angle falls within the rather narrow range of 128.7—132.5°; this suggests that hydrogen bonding strongly influences the degree of distortion. The most impressive evidence comes from the structures of the high- and low-temperature forms of $(PhCH_2CH_2NMeH_2)_2CuCl_4$ [46]. In the low-temperature form, which contains square coplanar $CuCl_4^{2-}$ ions, the mean NH···Cl distance is 3.31 Å, while in the high-temperature form, containing moderately distorted anions, the mean NH···Cl distance is 3.45 Å.

Hydrogen bonding is likely to affect bond lengths as well as bond angles. The mean distances quoted in Table 2 conceal the fact that the four Cu—Cl bonds may differ appreciably in length. Crystal forces may induce such distortions; in Cs_2CuCl_4 the bond lengths range from 2.220 Å to 2.244 Å, a difference of about 7 standard deviations. Larger differences are found in systems where hydrogen bonding may be important. A good example is found in $[(PNMe_2)_5H_2]CuCl_4 \cdot H_2O$ [26] where the Cu—Cl distances are 2.218, 2.251, 2.270 and 2.281 Å (all ± 0.003 Å). The shortest bond involves a Cl atom which is not involved in hydrogen bonding, while the longest-bonded Cl is only 3.19 Å from a protonated N atom. The Cl atoms at 2.251 and 2.270 Å are respectively, 3.26 Å and 3.31 Å from the water O atom. However, in $(NMe_3H)_3Cu_2Cl_7$ [70] the situation is less straightforward. The symmetry of the anions is actually closer to C_{3v}, with a very small angular distortion from T_d. The Cu—Cl distances (±0.01 Å) are 2.20, 2.23, 2.23 and 2.30 Å. In this case, the longest Cu—Cl bond is associated with the only Cl atom not involved in hydrogen bonding; the other three are all within 3.5 Å of the protonated N atom. Crystal packing effects must be at least as important as hydrogen bonding in determining the relative Cu—Cl bond lengths, in this case at any rate.

(ii) Chlorocuprates(II) containing tetragonally-elongated $CuCl_6$ octahedra

Many tetrachlorocuprates(II), and at least one pentachlorocuprate(II), contain square coplanar $CuCl_4^{2-}$ ions which are linked to form infinite layers, as shown in Fig. 2. Each Cu atom forms four short Cu—Cl bonds (ca. 2.30 Å) and two long bonds (ca. 3 Å) so that the coordination geometry is a tetragonally-elongated octahedron. The $CuCl_4^{2-}$ ions are linked by essentially linear Cu—Cl—Cu bridges, one bond being short and the other long. A variant of this structure is found in $(Me_2CHNH_3)_2CuCl_4$, where the layers are cut into ribbons, held together by hydrogen bonding with the organic cations [69]. One-third of the copper atoms have tetragonal octahedral coordination, while the rest form D_{2d} $CuCl_4^{2-}$ ions with long (3.1—3.3 Å) contacts with a fifth Cl atom (see Table 2). Structural parameters for tetragonal octahedral $CuCl_6$ systems are summarised in Table 3.

There is little doubt that Cl atoms as far away as 3 Å are definitely bonded to the copper. Square coplanar, four-coordinate $CuCl_4^{2-}$ has a very different electronic spectrum from that of the tetragonal octahedral $CuCl_6$ chromophore, and orbital overlap is still appreciable at the long-bonded distance

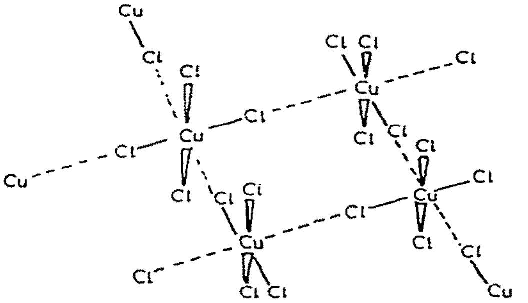

Fig. 2. Two-dimensional layer structure of anion in $(RNH_3)_2CuCl_4$.

TABLE 3

Structural parameters for chlorocuprates(II) which contain planar $CuCl_4^{2-}$ ions linked to form infinite sheets (R_S and R_L are the mean short and long Cu—Cl distances. Standard deviations are given in parentheses)

Compound	R_S (Å)	R_L (Å)	Ref.
$(NH_4)_2CuCl_4$	2.316(5)	2.793(5)	98
$(EtNH_3)_2CuCl_4$	2.281(5)	2.975(5)	99
$(n\text{-}C_3H_7NH_3)_2CuCl_4$	2.29(1)	3.04(1)	100
$(Me_2CHNH_3)_2CuCl_4$ [a]	2.282(10)	3.103(10)	69
	2.293(10)	3.071(12)	
$(PhNH_3)_2CuCl_4$	2.2906(5)	2.9178(5)	101
$(en)H_2CuCl_4$ [b]	2.295(3)	2.882(3)	102
$[Pt(NH_3)_4]CuCl_4$	2.287(4)	3.257(4)	103
$(dienH_3)CuCl_5$ [c]	2.274(7)	2.876(4)	104

[a] This compound also contains D_{2d} $CuCl_4^{2-}$ ions; see text and Table 2. There are two distinct tetragonal $CuCl_6$ moieties in the unit cell.

[b] en = 1,2-diaminoethane.

[c] dien = bis(2-aminoethyl)amine. One Cl^- per formula weight is not coordinated.

[97] (see also Sect. D). The arrangement of the $CuCl_4^{2-}$ ions in the layer compounds represents a definite polymerisation, and not merely a convenient mode of crystal packing.

We might expect to see some correlation between the equatorial (short) and axial (long) Cu—Cl bond lengths; the closer the axial ligands approach the metal, the greater should be the Cl—Cl repulsive forces and the equatorial bonds should lengthen. However, the equatorial distances in Table 3 cover the narrow range of 0.04 Å, with a mean standard deviation of 0.007 Å, so we cannot expect a very clear correlation. However, the longest equatorial distance is found in $(NH_4)_2CuCl_4$ which has the shortest axial bonds, and the Cu—Cl distance in square coplanar $CuCl_4^{2-}$ (see Table 2) is 2.265 Å, shorter than any of the equatorial bonds in Table 3.

In each $CuCl_4^{2-}$ ion in the compounds under consideration, two *trans* Cl atoms are involved in almost linear Cu—Cl—Cu bridging, while the other two may be regarded as terminal. Thus the two types of Cu—Cl equatorial bond should be different in length; this is found in practice, but the difference is usually rather small, and the equatorial bonds are often equal in length, within experimental error. In $(Me_2CHNH_3)_2CuCl_4$, the bonds to bridging chlorines are significantly shorter than those to non-bridging chlorines, but in $(PhNH_3)_2CuCl_4$ the reverse is the case.

All the cations listed in Table 3 contain RNH_3^+ cations and hydrogen bonding is likely to be important; N—Cl distances as short as 3.2 Å are commonly found, and each N atom makes eight or nine short contacts with Cl atoms. The possibilities for hydrogen bonding are certainly greater than in the systems listed in Table 2. It is tempting to speculate that this may be the factor which controls the preferred coordination geometry about the copper atoms in tetrachlorocuprates(II). The stronger the hydrogen bonding, the lower will be the charge on the Cl atoms, counteracting the effects of the shorter Cl—Cl distances as the tetrahedron is flattened, as discussed above. However, the bulk and shape of the cation are also important. Rb_2CuCl_4 is isostructural with $(NH_4)_2CuCl_4$ [14,105] and there is no hydrogen bonding here. The fact that Rb and NH_4 salts are frequently isomorphous is usually attributed to their similar size. The structure of K_2CuCl_4 is uncertain, but its electronic spectrum [17] suggests tetragonal octahedral coordination. If the long axial bonds do make a significant contribution to the stability of the system, the polymerisation of square coplanar $CuCl_4^{2-}$ ions to form infinite sheets with tetragonal octahedral coordination may be favourable, notwithstanding the preference of an isolated $CuCl_4^{2-}$ ion for D_{2d} symmetry. The layer structure will be favoured if the cation is sufficiently small or flexible that it can fit easily between the layers and hold the overall structure together. It appears that all tetrachlorocuprates(II) with RNH_3^+ cations have essentially the same structure as $(NH_4)_2CuCl_4$ (provided that R is a straight-chain alkyl group), even up to R = $C_{10}H_{21}$. With R = Me_2CH, the sheets are cut into ribbons, reflecting the greater bulk and lower flexibility of the branched-chain cation. With still bulkier, inflexible cations (such as those found in the chlorocuprates(II) listed in Table 2), further disruption of the polymeric anion leads to the formation of discrete D_{2d} $CuCl_4^{2-}$.

(iii) Chlorocuprates(II) containing discrete $CuCl_5^{3-}$ ions

Mori et al. [8,106—109] in the early 1960's reported the preparation and properties of $[M(NH_3)_6]CuCl_5$ (M = Cr, Co). X-ray analysis [107] revealed discrete $CuCl_5^{3-}$ ions having almost regular trigonal bipyramidal geometry. Since five-coordination was still regarded as unusual at the time, and since the X-ray analysis was based on limited data and had a large *R* factor, the existence of D_{3h} $CuCl_5^{3-}$ was doubted for some time. A good deal of work was done in the mid-1960's on these pentachlorocuprates(II), as interest in five-coordination developed strongly [110—116]. Various spectroscopic studies failed to confirm or deny the existence of $CuCl_5^{3-}$ (see later sections on physical properties). In 1968, the trigonal bipyramidal anion was finally established by X-ray crystallography [117,118]. Since then, interest in these compounds has been focussed upon the details of the geometry of the anion. The equatorial bonds are appreciably longer than the axial bonds; R_{eq} is 2.3912(13) Å and 2.392(1) Å for the Cr and Co compounds, respectively, while the corresponding values of R_{ax} are 2.2964(12) Å and 2.295(1) Å. The mean Cu—Cl distance of 2.35 Å is appreciably greater than in $CuCl_4^{2-}$, as expected. The configuration of the anion raises two questions; why trigonal bipyramidal rather than square pyramidal, and why are the axial bonds shorter?

The problem of D_{3h} vs. C_{4v} geometry for five-coordinate systems is vexing

[110—116], even for closed-shell d^{10} species where we expect some guidance from the VSEPR model [119]. Thus we find trigonal bipyramidal $[CdCl_5]^{3-}$ but square pyramidal $[InCl_5]^{2-}$ [120,121]. Crystal field stabilization energy [122] favours square pyramidal coordination for Cu(II) but Gillespie [123] argues that appreciable covalency in the metal—ligand bond will favour the trigonal bipyramid. Angular overlap calculations [124—126] favour square pyramidal geometry for d^9 MX_5 complexes. However, there is usually little to choose between C_{4v} and D_{3h} for five-coordinate species and the two are often easily interconverted. The $CuCl_5^{3-}$ ion provides a classic example of a large, symmetrical, highly-charged anion which is stabilized in the lattice by a suitable counter-ion [127]. It would not be surprising if square pyramidal $CuCl_5^{3-}$ could be stabilized in a suitable lattice.

We now turn to the question of the relative bond lengths in the $CuCl_5^{3-}$ ion. In main group trigonal bipyramidal molecules and ions, the axial bonds are usually the longer; this may be easily rationalised [110] by considering the electrostatic repulsion between ligands. The argument can be extended to open-shell systems by the inclusion of crystal field effects. The hole in the d-shell in $CuCl_5^{3-}$ is in the d_{z^2} orbital, which interacts more strongly with the axial ligands. Thus repulsion between metal d-electrons and ligand electrons is lower along the three-fold axis, allowing the axial bonds to contract. It is further argued [117,123] that the contraction of the axial bonds for a D_{3h} d^9 system should be most marked if the ligands are relatively small, with only weak covalent bonding. This is supported by the crystal structure of $CuBr_5^{3-}$ [128]. The equatorial and axial bond lengths are, respectively, 2.5191(17) Å and 2.4500(22) Å; the axial contraction is smaller than in $CuCl_5^{3-}$. Angular overlap calculations [125] predict a stronger axial bond, as do extended Hückel calculations [65]. However, the structure of the $CdCl_5^{3-}$ ion is a little disquieting; electrostatic arguments suggest that a d^{10} trigonal bipyramidal system should have longer axial bonds, and extended Hückel calculations concur [129]. But the axial Cd—Cl bond is 0.037(10) Å shorter than the equatorial bonds. This may be compared with the shortening of 0.0691(39) found for $CuBr_5^{3-}$ where the bonds are comparable in length to those in $CdCl_5^{3-}$. We are led to consider how far crystal forces may contribute to the axial shortening. McGinnety [65,96] has discussed this problem, though his results are less certain than for $CuCl_4^{2-}$ since no force constant data are available for $CuCl_5^{3-}$. McGinnety concluded that electrostatic forces within the anion lead to a contraction of the axial bond by 0.002 Å, after making allowance for different charges on axial and equatorial ligands, although other assumed distributions could lead to a small axial elongation. However, a calculation of the crystal forces led to a contraction of the axial bonds by 0.1 Å. McGinnety concluded that an isolated $CuCl_5^{3-}$ ion would have five equal Cu—Cl distances of about 2.42 Å. These calculations must be regarded as more significant than the others we have mentioned, since the latter tend to predict shortening of the axial bond without attempting to estimate its magnitude.

There is no evidence to suggest that hydrogen bonding makes any contribution to the relative bond lengths in $CuCl_5^{3-}$. In the Cr compound, both axial and equatorial Cl atoms make short (3.31—3.40 Å) contacts with N atoms, but there is little to suggest that one is more strongly hydrogen-bonded than the other.

(iv) Chlorocuprates(II) containing dimeric $Cu_2Cl_6^{2-}$ ions

Most trichlorocuprates(II) contain the $Cu_2Cl_6^{2-}$ ion, with two bridging chlorines (Fig. 3). The Cu—Cl bonds within the dimer are relatively short, in the range 2.2—2.4 Å and the Cu—Cl—Cu bridging angle is about 95°. The dimers may be discrete and essentially isolated, with strict four-coordination of the copper, or they may be stacked to form infinite chains, with five- or six-coordination of the copper, and with long Cu—Cl bonds between adjacent dimers. Discrete $Cu_2Cl_6^{2-}$ ions tend to be appreciably non-planar; as the coordination number of the metal is raised to five and ultimately to six, the dimer approaches an essentially planar configuration. In Table 4 we collect structural data for $Cu_2Cl_6^{2-}$ ions; we divide the compounds into three classes, according to the coordination number of the copper. The two greatest Cl—Cu—Cl angles in the dimer give a good indication of its distortion from planarity. If both angles are close to 180° (as in $KCuCl_3$ and NH_4CuCl_3) the dimer is almost planar and the symmetry about the metal atom may be idealised as D_{4h}. If one angle is close to 180° and the other to 120° (as in $PhCH_2CH_2NMeH_2CuCl_3$), the coordination about the metal resembles a trigonal bipyramid with a vacancy in one of the equatorial positions (cf. main-group AB_4E molecules like SF_4); this position is occupied by a long-bonded Cl atom from a neighbouring dimer. If the two angles are approximately equal but considerably less than 180°, the coordination geometry can be described as a flattened tetrahedron of approximately D_{2d} symmetry, as in $CuCl_4^{2-}$.

PPh_4CuCl_3 and $AsPh_4CuCl_3$ contain discrete $Cu_2Cl_6^{2-}$ ions with strictly four-coordinate copper. The bond angles show that the dimer is appreciably distorted from planarity, and the coordination about the copper is a flattened tetrahedron (approximately D_{2d}). The terminal Cu—Cl bonds average 2.20 Å, a little shorter than the Cu—Cl bonds found in $CuCl_4^{2-}$ ions. The bridging Cu—Cl bonds are rather longer (as is always the case for $Cu_2Cl_6^{2-}$ dimers) and the average Cu—Cl bond length is 2.248 Å for PPh_4CuCl_3 and 2.263 Å for $AsPh_4CuCl_3$, typical values for four-coordinate copper in chlorocuprates(II). The longer bonds in $AsPh_4CuCl_3$ might be related to the greater size of the cation, which reduces the Madelung forces tending to compress the Cu—Cl

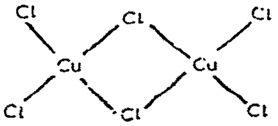

Fig. 3. The $Cu_2Cl_6^{2-}$ dimer.

TABLE 4

Structural parameters for chlorocuprates(II) which contain $Cu_2Cl_6^{2-}$ dimers, where the coordination number of the copper atoms is (a) 4, (b) 5 and (c) 6. (R_T and R_B are the Cu—Cl distances for terminal and bridging chlorines respectively, and R_L is the Cu—Cl bond length linking adjacent dimers. The angles θ are the two greatest Cl—Cu—Cl angles in the dimer. Standard deviations are given in parentheses)

Compound	R_T (Å)	R_B (Å)	R_L (Å)	θ (deg)	Ref.
(a)					
PPh_4CuCl_3	2.179(3)	2.292(2)	—	143.3(1)	130
	2.200(2)	2.321(2)		143.6(1)	
$AsPh_4CuCl_3$	2.198(3)	2.305(2)	—	145.2(1)	131
	2.215(2)	2.333(2)		144.6(1)	
(b)					
$Me_2NH_2CuCl_3$	2.249(5)	2.305(5)	2.733(6)	156.0(2)	132
	2.300(7)	2.346(6)		176.0(2)	
(pq)Cu_2Cl_6	2.238(3)	2.305(3)	2.668(3)	148.3(1)	133
	2.281(3)	2.330(3)		172.5(1)	
$PhCH_2CH_2$-$NMeH_2CuCl_3$	2.257(1)	2.306(1)	2.528(1)	133.0(1)	134
	2.283(1)	2.372(1)		176.7(1)	
(c)					
$KCuCl_3$	2.248(3)	2.314(3)	2.941(4)	173.2(1)	135
	2.267(3)	2.322(3)	3.113(4)	175.8(1)	
NH_4CuCl_3	2.25	2.32	2.99	172.8	135
	2.26	2.32	3.19	176.2	

bonds [65]. Although the terminal Cu—Cl bonds are appreciably shorter in these two compounds than in other trichlorocuprates(II), there is little variation in the bridging Cu—Cl distances. In PPh_4CuCl_3 and $AsPh_4CuCl_3$, the two bridging chlorines are chemically equivalent but the bridges are not symmetrical; the Cl atoms are not equidistant from the copper atoms.

The three five-coordinate species listed in Table 4 differ from one another in several respects. The stacking of the dimers in $Me_2NH_2CuCl_3$ is shown in Fig. 4. The coordination of the copper atoms may be described as a distorted

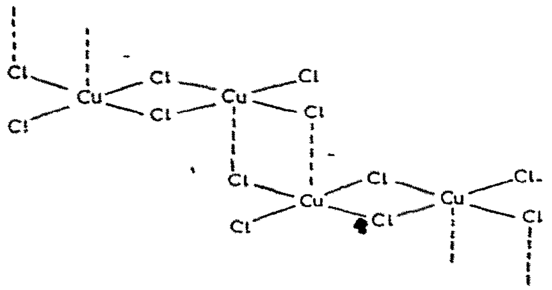

Fig. 4. Stacking of $Cu_2Cl_6^{2-}$ ions in $Me_2NH_2CuCl_3$.

square pyramid, closer to C_{2v} than C_{4v}. The long bonds linking the dimers into infinite chains involve two *trans* terminal chlorines in each dimer. The longer of the two terminal Cu—Cl distances is associated with the Cl atoms which form the long bonds. Although the Cu—Cl bridging bonds are similar in length to those in PPh_4CuCl_3 and $AsPh_4CuCl_3$, the terminal bonds are appreciably longer. This could be attributed to the smaller Cl—Cu—Cl angle made by the terminal chlorines in $Me_2NH_2CuCl_3$. Hydrogen bonding, while probably making a significant contribution to the stability of the overall structure, does not appear to affect the Cu—Cl bond lengths much. The shortest N—Cl contact (3.23 Å) involves the shortest-bonded chlorine (terminal), and Willett [132] suggests that this interaction is responsible for the distortion from C_{4v}. The longer-bonded terminal chlorines are 3.58 Å from the cation N atom and the bridging chlorines are no closer than 4.13 Å, greater than the sum of the van der Waals radii for N and Cl. The Cu—Cu distance within the dimer is 3.444(6) Å, rather greater than in PPh_4CuCl_3 and $AsPh_4CuCl_3$ (3.355 and 3.382 Å, respectively), as a consequence of the slightly larger Cl—Cu—Cl bridging angles in the latter. The shortest Cu—Cu distance between different dimers is 3.57 Å.

The stacking of the $Cu_2Cl_6^{2-}$ ions in $PhCH_2CH_2NMeH_2CuCl_3$ resembles that in $Me_2NH_2CuCl_3$, to the extent that the metal atoms are five-coordinate and two terminal Cl atoms at opposite ends of the dimer form long bonds with Cu atoms of neighbouring dimers. However, as shown in Fig. 5, the dimers are much more distorted from planarity. The ideal D_{4h} geometry about a Cu atom in a planar $Cu_2Cl_6^{2-}$ ion is distorted to C_{2v} in $Me_2NH_2CuCl_3$ by decreasing one *trans* Cl—Cu—Cl angle to 156° while leaving the other close to 180°; in $PhCH_2CH_2NMeH_2CuCl_3$, the smaller angle is reduced to 133°, and forma-

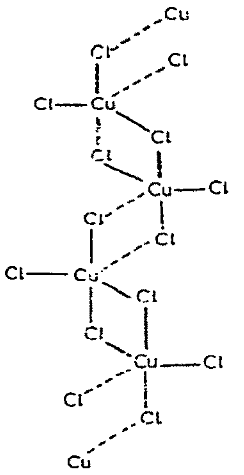

Fig. 5. Stacking of $Cu_2Cl_6^{2-}$ ions in $PhCH_2CH_2NMeH_2CuCl_3$.

tion of a long inter-dimer bond along the (approximately) two-fold axis completes a coordination geometry which may be described as a distorted trigonal bipyramid. The contraction of this bond angle allows closer approach of the long-bonded Cl atom, and the inter-dimer Cu—Cl distance is only 2.528 Å. The terminal Cu—Cl bonds which do not involve Cl atoms forming long inter-dimer links are appreciably shorter than those which do, as in $Me_2NH_2CuCl_3$. Again, as in $Me_2NH_2CuCl_3$ the shortest-bonded terminal chlorines are most deeply involved in hydrogen bonding; the H atoms have been located, and the relevant Cl—H distances are about 2.1 Å, consistent with a strong hydrogen bond. The other terminal chlorines are 2.7 Å away from the nearest NH hydrogen, while the bridging chlorines are no closer than 2.9 Å from a suitable hydrogen atom, about the same as the sum of the van der Waals radii. The Cu—Cu distance within each dimer is 3.45 Å and the closest Cu—Cu contact between different dimers is 3.55 Å, similar to the values found in $Me_2NH_2CuCl_3$.

The structure of $(pq)Cu_2Cl_6$ may be regarded as intermediate between those of $Me_2NH_2CuCl_3$ and $PhCH_2CH_2NMeH_2CuCl_3$. The Cl—Cu—Cl angles of 173° and 148° lead to a coordination geometry about half-way between the distorted square pyramid of $Me_2NH_2CuCl_3$ and the distorted trigonal bipyramid of $PhCH_2CH_2NMeH_2CuCl_3$, after the fifth long-bonded Cl is added; the long bond is 2.668 Å, intermediate between the values for the other two. No hydrogen bonding is likely in $(pq)Cu_2Cl_6$ but there is a relatively short (3.44 Å) contact between the shortest-bonded Cl atoms and a positively-charged N atom; Murray-Rust [133] attributes the distortion in the anion to this.

We now turn to the six-coordinate systems $KCuCl_3$ and NH_4CuCl_3. The stacking of the dimers in the crystal is shown in Fig. 6. Tetragonally-elongated octahedral coordination of the metal is completed by long axial bonds, one to a bridging chlorine of a neighbouring dimer and the other to a terminal chlorine of a different dimer; the latter bond is appreciably the shorter. The formation of these axial bonds does not seem to affect the bridging Cu—Cl bond lengths; they are about the same as in all the other species listed in Table 4. As usual, the shorter terminal Cu—Cl bond involves a chlorine which does

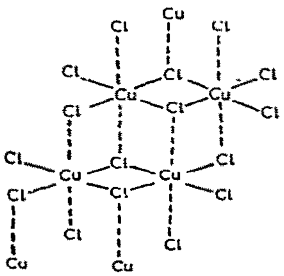

Fig. 6. Stacking of $Cu_2Cl_6^{2-}$ ions in $KCuCl_3$ and NH_4CuCl_3.

not form a long axial bond to the copper atom of a neighbouring dimer. It is significant that hydrogen bonding, although undoubtedly strong in NH_4CuCl_3, does not seem to affect the coordination geometry very much. The N atom is surrounded by 9 chlorines, at distances between 3.1 and 3.8 Å, but the structural parameters are about the same as for $KCuCl_3$, apart from the slightly longer axial bonds. Evidently the size of the cation is the dominant factor in determining the structure.

(v) Other chlorocuprates(II) with Cu—Cl—Cu bridges

Here we discuss the structures of four chlorocuprates(II) which have little in common with one another, or with any of the previously discussed systems, except that they involve Cu—Cl—Cu bridging.

$CsCuCl_3$ was the first chlorocuprate(II) to be analysed by X-ray diffraction [136] although this earlier structure was later refined considerably [137]. The structure can be described as containing infinite chains, formed by highly distorted $CuCl_6$ octahedra sharing faces. The coordination geometry about the metal is shown in Fig. 7; it may be described as an elongated octahedron, with unequal equatorial bond lengths of 2.281(6) and 2.355(4) Å, and an axial bond length of 2.776(6) Å. The chlorine atoms at a distance of 2.355 Å form symmetric Cu—Cl—Cu bridges, which we may denote as Cu(2.355)Cl(2.355)-Cu; the other bridges are Cu(2.281)Cl(2.776)Cu and Cu(2.776)Cl(2.281)Cu. The Cu—Cu distance is unusually short, 3.062 Å compared with about 3.4 Å in $Cu_2Cl_6^{2-}$. This arises from the small Cu—Cl—Cu bridging angles, which average 76° in $CsCuCl_3$ compared with about 95° in $Cu_2Cl_6^{2-}$. The Cu atoms form a spiral chain of 6_1 symmetry, and the short Cu—Cu distance raises the question of metal—metal bonding. However, overlap integral calculations [137] suggest that any direct Cu—Cu bond can be ruled out. The Cl—Cu—Cl angles average 90.2°, so that the short Cu—Cu distance arises from the small Cu—Cl—Cu angles which are an unavoidable consequence of a structure based on octahedra sharing faces.

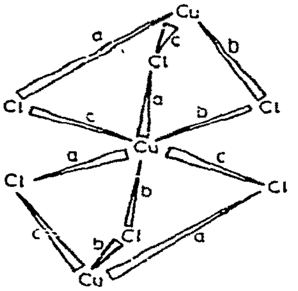

Fig. 7. Chain structure of the anion in $CsCuCl_3$.

Above 423 K, $CsCuCl_3$ has a somewhat different structure [138,139]. The site symmetry of the Cu atoms becomes C_{3v}, with two Cu—Cl distances of 2.39(1) and 2.51(1) Å. This may be regarded as a distortion of the $CsNiCl_3$ structure from D_{3d} to C_{3v} site symmetry, with the metal atom displaced towards one face of the octahedron. Thus the Cu—Cl—Cu bridges can be described as Cu(2.39)Cl(2.51)Cu. The bridging angle remains small (77.7°) and the Cu—Cu distance is still short (3.075 Å), though the spiral chain has disappeared; the space group has changed from $P6_122$ to $P6_3mc$.

Another example of a $(CuCl_3)_n^{n-}$ infinite chain is found [70] in $(Me_3NH)_3Cu_2Cl_7$. This compound has already been discussed since it also contains discrete $CuCl_4^{2-}$ ions. The $(CuCl_3)_n^{n-}$ chains are similar to those in $CsCuCl_3$ in that they can be described as distorted $CuCl_6$ octahedra sharing faces, but the octahedra are less symmetrical; the axial bond lengths are not significantly different, 2.70(1) and 2.72(1) Å, but the equatorial bonds are all different, 2.41(1), 2.39(1), 2.30(1) and 2.26(1) Å. Thus, as in $CsCuCl_3$, we can identify two long, two medium and two short bonds in the octahedron; but, in contrast to $CsCuCl_3$, the short bonds are *trans* to one another. The Cl—Cu—Cl axes in the octahedron are more nearly linear than in $CsCuCl_3$. The mean Cu—Cl—Cu angle is 79.2°, 3° more than in $CsCuCl_3$, leading to a greater Cu—Cu distance of 3.15 Å. The chain of Cu atoms is linear, in contrast to the 6_1 spiral chain in $CsCuCl_3$.

The structure of $(Me_3NH)Cu_2Cl_5$ has not been published in detail, but it is reported [140] to contain planar $Cu_4Cl_{10}^{2-}$ ions, formed by a chain of four Cu atoms with three μ-dichloro-bridges. The Cu—Cl bond lengths range from 2.17 to 2.41 Å, and the ions are stacked such that the terminal Cu atoms have square pyramidal five-coordination while the central metal atoms have tetragonal octahedral six-coordination. No doubt other $Cu_nCl_{2n+2}^{2-}$ ions will be identified in the future.

One of the most interesting chlorocuprates(II) to be studied in recent years is the compound originally [141] formulated as $[Co(en)_3]CuCl_5 \cdot H_2O$, but which has been found [142,143] to contain $Cu_2Cl_8^{4-}$ dimers. The configuration of the centrosymmetric anion is shown in Fig. 8. We may envisage the

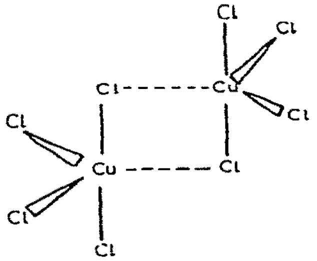

Fig. 8. Structure of the $Cu_2Cl_8^{4-}$ dimer.

structure as consisting of two highly-distorted trigonal bipyramids sharing an edge formed by joining one axial and one equatorial corner. The bridges can be described as Cu(2.703)Cl(2.325)Cu, and the bridging angle is 95.2°. The coordination geometry about the metal is remarkably similar to that in (pq)-Cu_2Cl_6 [133], discussed above. Inasmuch as the latter is considered to contain $Cu_2Cl_6^{2-}$ ions linked by long Cu—Cl bonds, it might be better to regard $[Co(en)_3]CuCl_5 \cdot H_2O$ as containing square planar $CuCl_4^{2-}$ ions, distorted to C_{2v} geometry, linked together in pairs by long Cu—Cl bonds.

Hydrogen bonding seems to be quite important in this compound. There are seven short NH···Cl contacts (3.15—3.41 Å) and O···Cl distances of 3.18, 3.28 and 3.30 Å. It is not clear how far this affects the coordination about the metal, but it is significant, perhaps, that the hydrogen bonding is stronger than in $[M(NH_3)_6]CuCl_5$.

(vi) Phase transitions in chlorocuprates(II)

The study of phase transitions in chlorocuprates(II) promises to be an area of major growth in the next few years. At one extreme, there are cases of abrupt, reversible, first-order phase transitions which involve a definite change in structure, as determined by atomic positions. At the other extreme, there are magnetic phase transitions, usually observable at very low temperatures; these will be discussed more fully in Sect. G. In between, there is a 'grey area' where physical properties change with temperature and pressure, sometimes discontinuously, but where there is little evidence for any real structural change.

We have already seen that $CsCuCl_3$ undergoes a phase transition at 423 K; this was first detected by Natarajan and Prakash, using differential thermal analysis, and was confirmed by X-ray crystallography [138,144,145]. Solid state physicists are deeply interested in such transitions, and in a number of cases it has been possible to associate them with low-frequency lattice vibrational modes ('soft modes') [146]. Kroese and Maaskant [139] have shown how the room-temperature structure of $CsCuCl_3$ can be derived from the high-temperature form by superimposing upon the latter a soft mode transforming as an irreducible representation of the high-temperature space group $P6_3mc$.

There has been much interest in the thermochromic properties exhibited by many chlorocuprates(II). Thus most compounds of the type $(RNH_3)_2CuCl_4$ are yellow at room temperature, but turn pale green on cooling and darken markedly on heating. This is a fairly gradual and continuous process, and it is not clear whether any definite phase changes are involved. Steadman and Willett [99] reported an endothermic transition in the differential thermal analysis curve of $(EtNH_3)_2CuCl_4$, but subsequent work [147] has failed to confirm this. Ferguson and Zaslow [104] have determined the crystal structure of $(dienH_3)CuCl_5$ at 20° and 120°; this compound exhibits the thermochromism typical of chlorocuprates(II) having the layer structure, being yellow at 20° and gold-brown at 120°. However, no significant changes in heavy-atom positions were detectable. There is the possibility that second-order phase transitions could be significant; Petzelt [148] has recently discussed the lattice dynamics of such transitions in $(RNH_3)_2CuCl_4$ systems.

In some cases, however, the thermochromism is so dramatic that it must be associated with a first-order phase transition. The most thoroughly studied system is $(PhCH_2CH_2NMeH_2)_2CuCl_4$ [46]; this compound is green at 25° and yellow at 80°, and accurate crystal structures have been obtained for both forms. These have already been discussed; the low-temperature form contains square coplanar $CuCl_4^{2-}$ ions, while the high-temperature form contains flattened tetrahedral $CuCl_4^{2-}$. $(Et_2NH_2)CuCl_4$ behaves similarly [147—149] and, although a full X-ray analysis has yet to be carried out, it would seem to be essentially isostructural with $(PhCH_2CH_2NMeH_2)_2CuCl_4$. Another definite phase change has been observed in $(Me_2CHNH_3)_2CuCl_4$ at 56° [147]. Electronic spectra indicate a shift towards tetrahedral geometry for all the Cu atoms in the high-temperature phase.

Pressure, as well as temperature, can induce phase transitions in chlorocuprates(II), as well as in a number of other transition metal compounds [150]. A simple example is the spectroscopic evidence [151] for a distortion towards square coplanar geometry of the anion in Cs_2CuCl_4 as the pressure is raised to 120 kbar. In $(Me_2CHNH_3)_2CuCl_4$, a new phase has been found at room temperature and 20 kbar pressure [152]; here, the flattened $CuCl_4^{2-}$ tetrahedra are further flattened towards square coplanarity, according to spectroscopic studies. No phase transition was observed in $(Et_2NH_2)_2CuCl_4$ up to 20 kbar.

The considerations which govern whether a tetrachlorocuprate(II) contains discrete D_{2d} anions or has the tetragonal octahedral layer structure at ambient temperature and pressure are likely to be relevant to phase changes under pressure. The application of pressure apparently assists inter-anion interaction in compounds containing D_{2d} tetrachlorocuprate(II) anions, leading to formation of the two-dimensional polymeric anion of the $(NH_4)_2CuCl_4$ structure. The lack of any pressure effect in $(Et_2NH_2)_2CuCl_4$ may arise from the fact that it already contains square coplanar, strongly hydrogen-bonded anions in its low-temperature form; however, Willett et al. [152] suggest on the basis of electronic spectra that the anion is somewhat distorted towards tetrahedral symmetry, and argue that further distortion towards square coplanarity and polymerisation is discouraged by the bulk of the secondary ammonium cations.

(vii) Summary of structural features

We conclude this section with some general remarks on the structures of chlorocuprates(II).

Compounds of the type $A'CuCl_3$ usually contain recognisable $Cu_2Cl_6^{2-}$ dimers. With large cations which do not allow inter-dimer interactions, the anions are appreciably non-planar, and the coordination geometry of the metal atoms resembles a flattened tetrahedron. With smaller cations, the dimers may become linked by long Cu—Cl bonds to form infinite chains, with five- or six-coordination of the copper. In the former case, the coordination geometry lies somewhere between a square pyramid and a trigonal bipyramid, and the dimer remains appreciably non-planar. With six-coordination, the copper atoms are in tetragonal octahedral environments and the dimers are essentially planar. $CsCuCl_3$ is rather an exceptional trichlorocuprate(II).

Tetrachlorocuprates(II) contain flattened tetrahedral $CuCl_4^{2-}$ ions if the cations are sufficiently bulky to prevent inter-anion contact, and do not offer many possibilities for hydrogen bonding which favours further flattening of the tetrahedron towards square coplanarity. With less bulky cations, notably of the type RNH_3^+, a two-dimensional layer structure is adopted in which square coplanar $CuCl_4^{2-}$ ions are linked by long Cu—Cl bonds, leading to tetragonal octahedral coordination. Hydrogen bonds of the type NH···Cl contribute to the stability of this structure, but the fact that it is also adopted by Rb_2CuCl_4 (and possibly by K_2CuCl_4) suggests that cation bulk is perhaps the dominant factor, and that copper(II) prefers tetragonal octahedral coordination in chlorocuprates(II), provided that the cations permit polymerisation. Where the cations are too bulky to allow layer formation, but hydrogen bonding is still important, square coplanar, four-coordinate $CuCl_4^{2-}$ ions may be present in a low-temperature phase. Heating disrupts the hydrogen bonding and there may be a reversion to a flattened tetrahedral anion in a high-temperature phase. Such behaviour may emerge as a feature of tetrachlorocuprates(II) with moderately large secondary ammonium cations.

Pentachlorocuprates(II) are likely to contain discrete D_{2d} $CuCl_4^{2-}$ ions and uncoordinated lattice chlorides if the cation is of the type which would normally stabilize such anions in a tetrachlorocuprate(II). Similarly, pentachlorocuprates(II) may contain tetragonal octahedral $CuCl_6$ chromophores if the cation is such as would favour the two-dimensional layer structure in a tetrachlorocuprate(II). Bulky, triply-charged cations such as $[M(NH_3)_6]^{3+}$ do not allow such polymerisation, and may stabilize the trigonal bipyramidal $CuCl_5^{3-}$ ion. An intermediate situation is found in $[Co(en)_3]CuCl_5 \cdot H_2O$, which contains distorted square planar $CuCl_4^{2-}$ ions linked together in pairs by long Cu—Cl bonds to form $Cu_2Cl_8^{4-}$ dimers, with five-coordinate copper.

Finally, we should make some mention of the role of the Jahn—Teller effect in the structural chemistry of chlorocuprates(II), using the term to describe structural distortions which might be predicted from the Jahn—Teller theorem without necessarily implying that the vibronic interactions explicitly discussed by Jahn and Teller [153] are wholly responsible. The effect appears strongly in the structures of chlorocuprates(II) having tetragonal symmetry. It seems clear that the angular distortion of the $CuCl_4^{2-}$ ion is an intrinsic property, associated with the d^9 configuration. The tetragonal distortion in the layer-type A_2CuCl_4 compounds must be similarly rationalised. Lohr [154,155] has discussed theoretically the Jahn—Teller effect in $CuCl_6^{4-}$ and in various binuclear chlorocuprate(II) anions, both real and imaginary.

D. LIGAND FIELD SPECTRA

This section deals with the d—d spectra of crystalline chlorocuprates(II), with emphasis on their value for routine structural diagnosis, and their interpretation in terms of ligand field theory. We begin with a brief account of the various experimental methods and theoretical approaches, and then proceed to a systematic account of chlorocuprate(II) d—d spectra with qualitative interpretation. Finally, we look at theoretical studies in more detail, and assess the relative merits of the various methods for the quantitative interpretation of d—d spectra.

Two earlier reviews cover the ligand field spectra of copper(II) compounds in general [4,156]. Readers who are not familiar with the general features of transition metal d—d spectra will find valuable accounts in the review by Ferguson [157] and the monograph of Lever [158].

(i) Experiment and theory

The transmission of plane-polarized light by oriented single crystals of known structure at low temperatures provides the most detailed information about the d—d spectra of non-cubic complexes [4,159]. Unfortunately, relatively little work of this kind has been done on chlorocuprates(II). Most of the spectra discussed in this section were obtained from diffuse reflectance or mull transmission spectra of polycrystalline material. Consequently, band assignments are less certain than for other copper(II) compounds and rely more heavily on theoretical predictions of the relative energies of d—d excited states. The simplest theoretical models for this purpose assume that, in the 'one-hole' d^9 configuration, we can equate optical transition energies to differences in orbital energies, so that the interpretation of a copper(II) d—d spectrum reduces to the problem of determining (qualitatively or quantitatively) the relative energies of the d-orbitals. Conventional ligand field arguments are useful, though not always unambiguous, for the routine assignment of a d—d spectrum. Chlorocuprates(II) have been extensively studied in the development of simple, empirical theories for the semi-quantitative calculation of ligand field splittings where the relative energies of the d-orbitals can be expressed in terms of about two freely-chosen parameters; if these parameters are deemed to depend only on the identities of the metal and the ligand (and perhaps also on the metal—ligand distances), the validity of the model can be tested rather thoroughly by applying it to the interpretation of chlorocuprate(II) spectra since such a wide range of coordination geometries and bond lengths are available. The point-charge crystal field model [160] and the angular overlap model [161] have proved rather successful (up to a point) in dealing with chlorocuprates(II). These empirical models are satisfying in that they are reasonably consistent (if not entirely realistic) in their approximations and assumptions. The assumption that optical transition energies in d^9 systems can be equated to differences in orbital energies is valid only if the relevant orbitals all have the same radial extension. In the crystal field model, this is consistent with the assumption that the orbitals concerned are simply the pure metal d-orbitals. In the angular overlap model, where the orbital splitting arises from covalency, the perturbation treatment assumes that the interaction between metal and ligand orbitals is very weak. Some more elaborate models lack this consistency; Wolfsberg—Helmholz semi-empirical MO calculations on transition metal complexes lead to a high degree of covalency in the highest occupied orbitals, and the extent of electron delocalisation can vary greatly amongst these orbitals. Hence, the calculation of d—d transition energies using such a model should require the explicit calculation of two-electron terms. This has seldom been done. We have shown [162,163] that the d—d spectra of tetragonal copper(II)ammine complexes can be explained by calculating two-electron terms within the INDO approximation, and subtracting these from the orbital energy differences obtained from the angular overlap model. Ab initio SCF calculations lead to orbital energies which are better defined than those obtained by semi-empirical methods, but which cannot be used directly for the calculation of transition energies [164]. These are best calculated by performing the SCF calculation on the ground state and on the relevant excited states, and taking the differences in total energy. Such differences are, of course, very small compared with the total energies involved and there must be some doubt as to whether the inherent deficiencies of the Hartree—Fock method are sufficiently unimportant (or are adequately compensated) to allow reasonably accurate predictions of d—d transition energies of of ca. 1 eV.

In the account of chlorocuprate(II) spectra which follows, we attempt only simple qualitative theoretical interpretations, using conventional ligand field arguments; more elaborate theories, which seek to calculate d—d transition energies, will then be discussed and their application to chlorocuprates(II) assessed.

(ii) The tetrachlorocuprate(II) ion $CuCl_4^{2-}$

The d—d spectra of compounds which are known (or believed) to contain discrete $CuCl_4^{2-}$ ions are summarised in Table 5. The D_{2d} $CuCl_4^{2-}$ ion, with a typical tetragonal flattening ($\theta = 120$—$140°$), usually shows two d—d bands in the near-IR, at about 9 kK and 6 kK, as shown in Fig. 9. This spectrum may be rationalised in terms of the qualitative crystal field splitting diagram (Fig. 10) which shows how the d-orbitals are expected to behave under a distortion from T_d, through D_{2d}, towards D_{4h} as a tetrahedron is flattened. For a moderately flattened tetrahedron, the ground state is evidently $^2B_2$, with excited states ^2E, $^2B_1$, $^2A_1$. This ordering was established experimentally by Ferguson [165] using single crystals of Cs_2ZnCl_4 coated with Cs_2CuCl_4, with polarized light at low temperatures. Since the tetrahedral e orbitals are not expected to be split by a large amount (except for grossly flattened tetrahedra), the $^2B_1$ and $^2A_1$ states are rarely resolved; the $^2B_2 \rightarrow {}^2B_1$ transition is electron-

TABLE 5

Ligand field spectra of discrete $CuCl_4^{2-}$ ions

Compound	*E* (kK)	*T* (K)	Method	Ref.
Cs_2CuCl_4	9.05, 7.90, 5.55, 4.80	20	SCP	165
$Cs_2Zn(Cu)Cl_4$	8.69, 7.50, 5.21, 4.45	77	SCP	92
$(NMe_4)_2CuCl_4$	9.0, 6.0	298	R	166
	9.22	298	F	167
$(NEt_4)_2CuCl_4$	8.93	298	F	167
$(Me_2NH_2)_2CuCl_4$	9.20, 5.75	78	F	147
	9.22	298	F	167
$(Me_2NH_2)_3CuCl_5$	10.7, 7.3	78	F	147
	9.52	298	M	72
$(Me_2CHNH_3)_2CuCl_4$	10.0	330	F	147
$(n\text{-}Bu_4N)_2CuCl_4$	9.43	298	R	168
$(Et_3NH)_2CuCl_4$	9.39	298	F	167
$(Et_2NH_2)_2CuCl_4$	10.2, 7.3	317	F	147
	9.5, 8.0	338	R	149
	16.0, 11.3, 9.5	298	R	149
	15.3, 12.9, 9.9	9	F	147
$(PhCH_2NMe_3)_2CuCl_4$	8.85, 5.92	298	SCP	169
	9.30	298	F	167
$(PhMe_3N)_2CuCl_4$	9.26	298	F	167
$(PhCH_2CH_2NMeH_2)_2CuCl_4$	9.1	363	M	46
	16.1, 13.6, 11.5	298	M	46
	16.9, 14.3, 12.5	77	M, SCP	46, 170
$(PhCH_2CHMeNMeH_2)_2CuCl_4$	10.2	298	M	72
$(pq)CuCl_4$	10.0	298	R	171
$(quinH)_2CuCl_4$	8.16	298	F	167
$(nicH)_2CuCl_4$	7.75	298	F	167
$(PPh_4)_2CuCl_4$	7.97	298	F	167
$24DMBDCuCl_4$	8.3, 5.1	298	R	172
$2478TMBDCuCl_4$	10, 7	298	R	173
$2M4PhBDACuCl_4$	8, 5	298	R	173

Note: All measurements made at 'room temperature' or at an unspecified temperature are assumed to have been taken at 298 K. The following abbreviations have been used: SCP = single crystal polarized spectrum; M = mineral oil mull transmission spectrum; R = diffuse reflectance spectrum; F = spectrum taken of thin film after evaporation of solvent. quin = quinoline; nic = nicotine; pq = *N,N'*-dimethyl-4,4'-bipyridinium; 24DMBD = 2,4-dimethyl-1H-1,5-benzodiazepinium; 2478TMBD = 2,4,7,8-tetramethyl-1H-1,5-benzodiazepinium; 2M4PhBD = 2-methyl-4-phenyl-1H-1,5-benzodiazepinium.

ically forbidden, so that the band at ca. 9 kK may be assigned to the $^2B_2 \rightarrow {}^2A_1$ transition, with the $^2B_2 \rightarrow {}^2B_1$ transition lying nearby. Spin-orbit coupling should split the ^2E state by λ, which is about 0.5 kK for chlorocuprates(II). This splitting only appears in single crystals with different polarizations at low temperatures, and may be enhanced by second-order effects, distortions from strict D_{2d} geometry and dynamic effects. The $^2B_2 \rightarrow {}^2E$ transition is

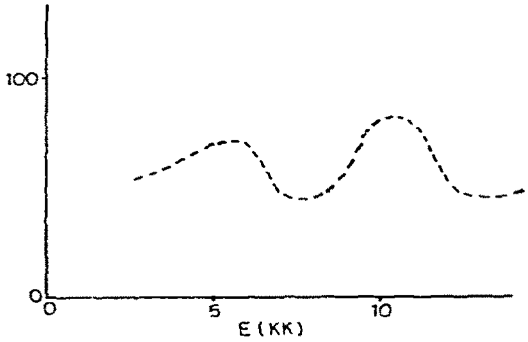

Fig. 9. d–d spectrum of the D_{2d} $CuCl_4^{2-}$ ion.

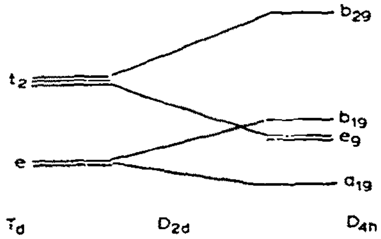

Fig. 10. d-orbital splitting as a tetrahedral system is flattened through D_{2d} and ultimately to D_{4h} symmetry.

found around 6 kK, where it may be obscured by vibrational overtones and combination bands of a complex cation. The absolute intensities of the bands have rarely been measured. The 9 kK band apparently has a molar extinction coefficient of about 120 l mol^{-1} cm^{-1}, consistent with a d–d band in a non-centrosymmetric copper(II) system. The lower energy band is usually somewhat weaker at room temperature, but intensifies markedly on cooling. Both bands move to higher energy at low temperatures, as is usual for d–d transitions.

The assignment of the d–d transitions in compounds containing square coplanar $CuCl_4^{2-}$ ions has yet to be established. At low temperatures, bands are observed at *ca.* 17, 14 and 12 kK in $(PhCH_2CH_2NMeH_2)_2CuCl_4$ [46,170]. The polarization data [170] are unconclusive, though the slight polarization of the central band suggests that it could be the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition; this would be in conflict with the predictions of ligand field theory, as we shall discuss further at the end of this section. On intensity grounds, we feel inclined to assign the central band (the most intense) to $^2B_{1g} \rightarrow {}^2E_g$ (analogous to $^2B_2 \rightarrow {}^2E$ in D_{2d}) and ligand field arguments suggest that the $^2B_{2g}$ state should lie lower in energy than ^2E_g, so that the 12 kK band is assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$. Thus the 17 kK band must be $^2B_{1g} \rightarrow {}^2A_{1g}$. This ordering is not inconsistent with qualitative arguments, though, as we shall see later, there are some difficulties in explaining these relative energies semi-quantitatively. However, the similarity between the spectrum of D_{4h} $CuCl_4^{2-}$ and that of square coplanar CuO_4 chromophores is rather impressive (allowing for the higher transition energies expected for oxygen-donor ligands), and in the latter case there seems to be agreement that the highest energy band is the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition [156,174,175]. The d–d spectrum of $(Et_2NH_2)_2CuCl_4$ is rather similar to that of $(PhCH_2CH_2NMeH_2)_2CuCl_4$, though with the bands shifted to slightly lower energies; this may reflect a small distortion towards tetrahedral geometry [147,149]. A noteworthy feature of the $(PhCH_2CH_2NMeH_2)_2CuCl_4$

spectrum measured with single crystals at low temperatures is the vibrational structure observed [170]; the spacing is consistent with the Cu—Cl stretching frequency of about 265 cm^{-1}.

There have been a number of attempts to relate the *d*—*d* absorption maxima in $CuCl_4^{2-}$ ions to the flattening angle θ, on a purely empirical basis. Willett et al. [147] found smooth curves when the energies of the two prominent *d*—*d* bands were plotted against θ for compounds of known (or suspected) structure. Unfortunately, they took $[Pt(NH_3)_4]CuCl_4$ as an example of a compound containing square coplanar $CuCl_4^{2-}$ ions, and it is now known [103] that the copper atom in this compound has tetragonal octahedral coordination. Moreover, Willett et al. took the average energy of the two highest-energy bands in this compound, and used older crystallographic data [75,176] for Cs_2CuCl_4 which quote a smaller value of θ than that now accepted [65]. Harlow et al. [72] have found a linear correlation between the highest-energy band position and including data for non-planar $Cu_2Cl_6^{2-}$ ions and taking care to use spectra measured at 298 K throughout. The equation of the straight line is $E = (0.1445\theta - 9.784)$ kK. Unfortunately, 7 of the 8 compounds concerned have θ values in the narrow range 129—145°, the eighth being square coplanar $CuCl_4^{2-}$ ($\theta = 180°$). But for the last of these, the correlation would not be very convincing. Moreover, the equation of the straight line predicts that a regularly tetrahedral $CuCl_4^{2-}$ ion would have Δ_t = 6.05 kK, about twice as great as the values found for $CoCl_4^{2-}$ and $NiCl_4^{2-}$ [177—179]. If this linear correlation is to be used in order to predict the geometries of $CuCl_4^{2-}$ ions in compounds of unknown structure, more points will be needed on the graph, and the problem of the *d*—*d* spectrum of square planar $CuCl_4^{2-}$ will need to be cleared up, since such a correlation requires an assurance that the transition energy used corresponds to the same excited state in all cases. We suspect that, in fact, the highest-energy *d*—*d* transition is always $^2B_2 \rightarrow {}^2A_1$ ($^2B_{1g} \rightarrow {}^2A_{1g}$ in D_{4h}).

Another correlation has been proposed by Lamotte-Brasseur [167], who uses the expression

$$D = (L_3 - L_1)/(L_1 + L_2 + L_3)^{1/3}$$

as a measure of the tetragonal distortion, where L_1, L_2 and L_3 are the shortest distances between two opposite edges of the distorted tetrahedron, with $L_1 < L_2 < L_3$. For five systems of known structure (though, in two cases, using data which are now considered obsolete) a linear correlation was found between the *d*—*d* maximum (in nm) and D. But three compounds of unknown structure (and with abnormally low *d*—*d* transition energies) do not fall on the straight line.

(iii) Compounds containing tetragonal octahedral $CuCl_6$ chromophores

The *d*—*d* spectra of compounds having the layer-type structure arising from polymerisation of square planar $CuCl_4^{2-}$ ions are listed in Table 6. We include

TABLE 6

Ligand field spectra of chlorocuprates(II) containing tetragonal octahedral $CuCl_6$ chromophores

Compound	*E* (kK)	*T* (K)	Method	Ref.
$CuCl_2$	12.2	298	R	181
$CsCuCl_3$	11.8, 11.0 -	298	R	182
	13.10, 12.75, 10.0, 8.3	7	SCP	183
$(MeNH_3)_2CuCl_4$	13.0, 10.7	77	SC	166
	13.3, 12.2, 10.8	77	SC	184
$(EtNH_3)_2CuCl_4$	12.8, 10.5	77	SC	166
$[Pt(NH_3)_4]CuCl_3$	14.3, 13.1, 10.9	298	M	181
$(dienH_3)CuCl_5$	12.50, 11.36	298	R	185
	12.99, 11.36	77	R	185

SC = single crystal (unpolarized) spectrum. Other abbreviations are as given for previous tables.

in the table $CuCl_2$, whose structure [180] consists of chains of Cu atoms linked by Cu—Cl—Cu μ-dichloro-bridges, stacked so as to complete tetragonal octahedral coordination of the metal atoms; the equatorial and axial bond lengths are 2.30 and 2.95 Å, respectively. We also include $CsCuCl_3$, where there are three quite distinct bond lengths. All the other compounds in Table 6 have the $(NH_4)_2CuCl_4$ layer structure.

The *d—d* spectrum of a typical compound of this type is shown in Fig. 11. The band at about 13 kK may be assigned to the $^2B_{1g} \rightarrow {}^2E_g$ transition but the assignment of the remainder of the spectrum is rather doubtful. The polarization data for $CsCuCl_3$ [183] are not particularly helpful in completing the assignment. Qualitative arguments suggest the relative energies

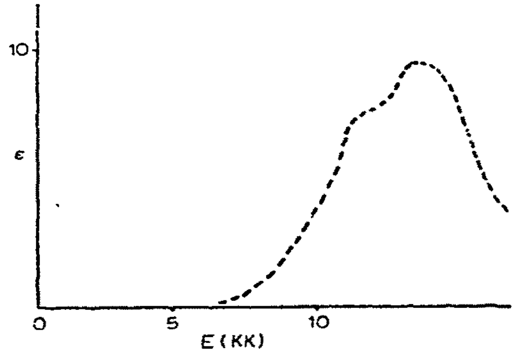

Fig. 11. *d—d* spectrum of the tetragonal octahedral $CuCl_6$ chromophore.

$d_{x^2-y^2}(b_{1g}) > d_{z^2}(a_{1g}) > d_{xy}(b_{2g}) > d_{xz,yz}(e_g)$, but d_{z^2} could easily lie below d_{xy}, depending on how much the axial ligands contribute to the field. The band (or shoulder) seen around 11 kK could arise from either the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ or ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, or, more likely, from the superimposition of the two. The possibility that the ${}^2A_{1g}$ state may lie at much lower energy (ca. 5 kK) has been considered, but diligent searches have failed to find any electronic transitions in this region [166,184], which is liable to be obscured by organic cation absorption. All the $d-d$ bands in $CsCuCl_3$ lie between 8 and 13 kK [183] and there can be no interference of the lower-energy region here. $CsCuCl_3$ has the shortest axial bond length of all the systems in Table 6: the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition should be most sensitive to the degree of axial elongation, and should be found at lower energy in $CsCuCl_3$ than elsewhere. Hence the 8.3 kK band in $CsCuCl_3$ may be assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition (assuming approximate D_{4h} symmetry), and the 10.0 kK band to ${}^2B_{1g} \rightarrow {}^2B_{2g}$. The former transition should lie at higher energy in the other compounds, while the latter should not vary much with tetragonality.

In $(MeNH_3)_2CuCl_4$, three peaks have been observed [184] between 10 and 14 kK. It could be argued that both bands at 12.2 and 13.3 kK arise from the ${}^2E_g$ state, which is split to first-order by spin-orbit coupling by λ, about 0.5 kK. This splitting could be increased by second-order interactions only if the ${}^2A_{1g}$ state lies just below ${}^2E_g$ in energy and ${}^2B_{2g}$ lies much lower [156]. This situation seems unlikely; all the evidence points to the ${}^2A_{1g}$ and ${}^2B_{2g}$ states being quite close together, but we are unable to decide which is which in the spectrum. Three bands are also observed in the spectrum of $[Pt(NH_3)_4]CuCl_4$ [181]. This is the most elongated system of the compounds in Table 6, and it would seem reasonable to assign the 10.9 kK band to the ${}^2B_{2g}$ state, on the grounds that this transition should be relatively insensitive to the degree of tetragonal distortion.

(iv) The $CuCl_5^{3-}$ ion

Ligand field spectra of compounds known (or believed) to contain the trigonal bipyramidal $CuCl_5^{3-}$ ion are given in Table 7. At room temperature, a peak at about 8 kK with a shoulder around 10 kK are observed (Fig. 12). On cooling, the absorption moves to higher energy and the peaks are better resolved.

Simple ligand field arguments suggest the relative energies $d_{z^2}(a_1') > d_{xy,x^2-y^2}(e') > d_{xz,yz}(e'')$. The ground state is evidently ${}^2A_1'$, with excited states ${}^2E'$ and ${}^2E''$. No polarization data can be obtained since the crystals are invariably cubic, but the assignment of the 8 kK band to ${}^2A_1' \rightarrow {}^2E'$ and the 10 kK band to ${}^2A_1' \rightarrow {}^2E''$ seems reasonably well established. The former is electronically allowed and the latter forbidden, in keeping with the relative intensities. It is argued [185] that the ${}^2A_1' \rightarrow {}^2E''$ transition should be more affected by cooling than the ${}^2A_1' \rightarrow {}^2E'$ transition, and the shifts in band positions between 298 and 77 K would therefore support the

TABLE 7

Ligand field spectra of chlorocuprates(II) containing the $CuCl_5^{3-}$ ion

Compound	E (kK)	T (K)	Method	Ref.
$[Co(NH_3)_6]CuCl_5$	10.2, 8.4	298	SC	186
	10.10, 8.40	298	R	185
	10.25, 8.50	298	R	187
	10.81, 8.88	77	R	185
	10.4, 8.2	77	M	181
$[Cr(NH_3)_6]CuCl_5$	10.00, 8.33	298	R	185
	10.81, 8.70	77	R	185
$[Rh(NH_3)_6]CuCl_5$	9.90, 8.26	298	R	185
	10.99, 9.01	77	R	185
$[Ru(NH_3)_6]CuCl_5$	10.20, 8.50	298	R	185
	10.81, 9.01	77	R	185

above assignment. However, the validity of this argument has been questioned [117]. There has been the suggestion [181] that the $^2A_1' \rightarrow {}^2E'$ transition may lie at low energy, obscured by vibrational absorption of the cations, and that the double peak may arise from splitting of the $^2E''$ state by spin-orbit coupling and a dynamic Jahn—Teller effect. But spin-orbit coupling alone (and with the ^2E state well removed to preclude significant second-order effects) cannot split the $^2E''$ state by more than about 0.5 kK, and there seem to be no cogent reasons for rejecting the assignment of the 8 kK band to the $^2E'$ state.

(v) $Cu_2Cl_6^{2-}$ dimers

Published *d—d* spectra of chlorocuprates(II) containing recognisable $Cu_2Cl_6^{2-}$ dimers are listed in Table 8. In PPh_4CuCl_3 and $AsPh_4CuCl_3$, which contain discrete, non-planar $Cu_2Cl_6^{2-}$ ions, the environment of the metal atom closely resembles that in D_{2d} $CuCl_4^{2-}$ ions, and the *d—d* spectra may be inter-

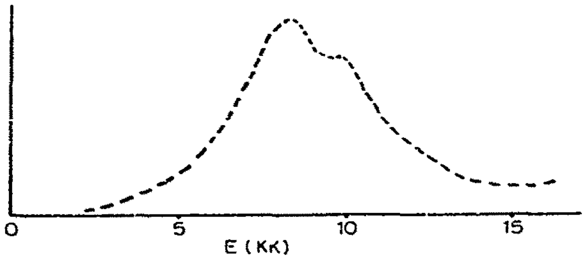

Fig. 12. *d—d* spectrum of the D_{3h} $CuCl_5^{3-}$ ion.

TABLE 8

Ligand field spectra of compounds containing $Cu_2Cl_6^{2-}$ dimers

Compound	E (kK)	T (K)	Method	Ref.
PPh_4CuCl_3	11.1, 8.0	298	R	168
	11.25	298	M	72
$AsPh_4CuCl_3$	11.1, 8.5	298	R	168
	12.20, 8.93	78	SC	131
$N(n\text{-}Bu)_4CuCl_3$	11.0, 7.8	298	R	168
$[MgCl(DIMP)(H_2O)_4]CuCl_3$	11.0	298	M	23
$(nmpH)CuCl_3$	10.60, 7.69	298	M	134
	11.10, 9.17, 7.52	77	M	134
$(pq)Cu_2Cl_6$	10.0	298	R	171
$KCuCl_3$	12.9, 10.5	298	SC	188
$Me_2NH_2CuCl_3$	12.9, 10.8	298	SC	188
$Me_2CHNH_3CuCl_3$	12.5, 11.5	298	SC	188

nmpH = $PhCH_2CH_2NMeH_2$; DIMP = diisopropyl methylphosphonate; n-Bu = $n\text{-}C_4H_9$. (other abbreviations are as used in previous Tables).

preted along similar lines. These compounds fit quite nicely into the correlations which have been proposed between d—d absorption maxima and the flattening angle θ in D_{2d} systems [72,147,167].

The spectra of $KCuCl_3$ is very similar to those of other chlorocuprates(II) containing tetragonal octahedral $CuCl_6$ chromophores, such as are summarised in Table 6. The rather different coordination geometry in $Me_2NH_2CuCl_3$ does not appear to influence the d—d spectrum. The spectra of the other compounds of known structure listed in Table 8 are more difficult to discuss. The symmetry of the coordination sphere is rather low and it is not easy to present any simple assignment of the bands. However, it is interesting to note the similarity between the band positions in $(PhCH_2CH_2NMeH_2)CuCl_3$ and in $CuCl_5^{3-}$, although the former contains a grossly distorted trigonal bipyramidal arrangement about the metal.

We have included in Table 8 $N(n\text{-}C_4H_9)_4CuCl_3$ and $[MgCl(DIMP)(H_2O)_4]$-$CuCl_3 \cdot DIMP$ (DIMP = diisopropyl methylphosphonate), whose structures are unknown. It would be helpful if d—d spectra could easily distinguish the various structural types encountered in trichlorocuprates(II), but the available data are not encouraging. The spectra of these two compounds can scarcely be distinguished from those of MPh_4CuCl_3 (M = P, As) and $(PhCH_2$-$CH_2NMeH_2)CuCl_3$. More spectra and more structures will be required before it is possible to make much use of d—d spectra for routine structural diagnosis of trichlorocuprates(II).

(vi) Other systems

Here we look at the $Cu_2Cl_8^{4-}$ dimer, and gaseous, molecular $CuCl_2$.

The near-IR spectrum of $[Co(en)_3]CuCl_5 \cdot H_2O$ shows a broad maximum at 10.8 kK with a shoulder at 10.0 kK [142,143]. The relatively low symmetry in this ion should produce more bands but these have yet to be resolved and there is little profit in any attempt to interpret this spectrum until more data are available. At any rate, the spectrum is unique amongst chlorocuprates(II), and this could be helpful in identifying the dimer should it appear in another compound.

The properties of molecular $CuCl_2$ are clearly of some relevance to chlorocuprates(II). The gaseous molecule is believed to be linear, and qualitative ligand field arguments indicate the energy sequence $d_{z^2} > d_{xz,yz} > d_{xy,x^2-y^2}$. Thus we expect two *d—d* transitions, $^2\Sigma_g \rightarrow {}^2\Pi_g$ and $^2\Sigma_g \rightarrow {}^2\Delta_g$. Hougen et al. [189] reported bands at 9.0 and 18.0 kK which were assigned respectively to these transitions. However, the 18 kK band was rather intense ($\epsilon \sim 500$ l mol^{-1} cm^{-1}) and it was suggested that this was more likely to be a charge transfer band [190]. Subsequent work [191] placed the higher energy band at 19.0 kK, with $\epsilon = 3000$ l mol^{-1} cm^{-1}, indicating the assignment of the 9 kK band to $^2\Sigma_g \rightarrow {}^2\Delta_g$, while the $^2\Sigma_g \rightarrow {}^2\Pi_g$ transition was believed to be below 4 kK, outside the spectral range measured; a slight increase in intensity was noticed between 5 and 4 kK. Calculations [192] suggest that the $^2\Sigma_g \rightarrow {}^2\Pi_g$ transition should lie near 9 kK, where a band is indeed observed, with the $^2\Sigma_g \rightarrow {}^2\Delta_g$ transition at about 16 kK where it would be obscured by the broad, intense charge transfer absorption centred on 19 kK. However, Lever and Hollebone [193], in a detailed and critical discussion of the spectra of MCl_2 molecules prefer the assignment of DeKock and Gruen [191], on the grounds that the *d*-orbital splitting parameters required by this assignment are more consistent with those which fit the *d—d* spectra of other MCl_2 species. They did not explore the consistency of their splitting parameters with those required in other chlorocuprates(II).

(vii) Quantitative interpretation of chlorocuprate(II) d—d spectra

Here we survey theoretical work which has sought to calculate *d—d* transition energies in chlorocuprates(II). At the beginning of this section, we discussed briefly some features of the various theoretical studies. These will now

(a) Point charge crystal field model

Here we consider [illegible] perturbation of the metal *d*-orbitals by point charges located at the ligand nuclei. The relative energies of the *d*-orbitals can be expressed [160,194—197] in terms of the radial parameters a_2 and a_4, where $a_n = q\langle r^n\rangle/R^{n+1}$. q is the magnitude of the negative point charge deemed to reside on the ligands, $\langle r^n\rangle$ is the mean value of the nth power of the distance of a *d*-electron from the nucleus and R is the metal—ligand distance. The a_n can be calculated explicitly from SCF wave functions, but these lead to quite unrealistic orbital splittings. Furlani et al. [169,184] calculated the radial parameters from Slater-type functions with arbitrarily chosen exponents but the results were not very satisfactory. It seems best to regard a_2 and a_4 as freely-chosen parameters, proportional to R^{-3} and R^{-5} respectively, and hope that a single value of each (adjusted to take account of different values of R) will successfully fit the d—d spectra over a range of different compounds. This, of course, assumes that the d—d transition energies can be directly equated to orbital energy differences, as discussed above under (i). Several calculations of this type have been reported for chlorocuprates(II) [181,182,189,191,196,197], and in most cases d—d transition energies could be calculated to within about 10% of their observed values. Unfortunately, many of the crystallographic data on which the calculations were based have since been superseded, and little care was taken to use d—d spectra taken at the same temperature in all compounds. It is evident from Tables 5—8 that the transition energies are appreciably temperature-dependent. If we repeat the earlier crystal field calculations using the latest X-ray data and restrict ourselves to spectroscopic work done at a uniform temperature (say 77 K) the results are rather less convincing. Moreover, the parameters required to fit the spectrum of molecular $CuCl_2$, whether we accept the assignment of Hougen et al. [189] or that of De Kock and Gruen [191], are very different from those which apparently fit the spectra of chlorocuprates(II); this could arise from the inadequacy of the assumed R^{-3} and R^{-5} dependence of the radial parameters a_2 and a_4. The crystal field calculations for tetragonal octahedral $CuCl_6$ chromophores place the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition at about 5—6 kK, while all the experimental evidence suggests that it lies much higher in energy, again suggesting that the model fails to give an adequate measure of the radial dependence of the parameters. Finally, the parameters used to fit the spectra of chlorocuprates(II) in these early calculations fail to predict the spectrum of square coplanar $CuCl_4^{2-}$. Hatfield and Piper [181] took $Pt(NH_3)_4CuCl_4$ to contain this D_{4h} anion, but a recent X-ray analysis [103] shows that the compound has tetragonal octahedral $CuCl_6$ chromophores. Thus the early successes of the crystal field model were somewhat fortuitous, being based on incomplete (even inaccurate) spectroscopic and structural information, and the model has failed to stand the test of further experimental work.

(b) Angular overlap model

This approach, essentially an empirical MO theory, was applied to chlorocuprates(II) a little later than the crystal field model, and appeared to remedy some of the deficiencies of the latter. Although it has had its failures, the angular overlap model has proved more amenable to refinement and refurbishment than the crystal field model; these refinements have necessarily diminished its utility in the sense that new parameters have had to be introduced and the model has become more cumbersome.

The model supposes that the splitting of the ligand field orbitals arises from covalent bonding. The destabilization of a d-orbital as a consequence of its becoming weakly antibonding is proportional to the square of the appropriate group overlap integral. The relative energies of the ligand field orbitals can be written down as multiples of the parameters e_σ and e_π. For a d^9 system, it is assumed that the d—d transition energies are given by the appropriate orbital energy differences. The parameters e_σ and e_π are taken to be proportional to the squares of the respective diatomic overlap integrals, so that their radial dependence can be gauged by overlap integral calculations, as can their relative magnitudes, provided that σ-antibonding destabilization is assumed to arise solely from interactions with ligand *np*-orbitals. The earliest application of the model to chlorocuprates(II) [198] neglected π-bonding, and led to a reversal of the correct relative energies of the $^2A_1$ and $^2B_1$ states in the D_{2d} $CuCl_4^{2-}$ ion. The model was then refined to include π-bonding and purely crystal field effects, and applied with some success to D_{4h}, D_{3h}, D_{2d} and $D_{\infty h}$ systems [192,193,199,200]. However, the model suffers from the same defects as the crystal field model, though to a lesser degree. The $^2B_{1g} \rightarrow {}^2A_{1g}$ transition energy in tetragonal octahedral systems is still somewhat underestimated and the model fails to account for the spectrum of square coplanar $CuCl_4^{2-}$. Depending on which assignment one prefers, the model may be seriously in error for molecular $CuCl_2$. These problems can be largely resolved by the introduction of additional parameters to allow for *d*—*s* and *d*—*p* mixing [201]. For example, the spectrum of square coplanar $CuCl_4^{2-}$ can be accounted for if the d_{z^2} orbital is stabilized by some 6 kK by mixing with the 4*s*-orbital. If the d_{z^2} orbital in molecular $CuCl_2$ is similarly stabilized by some 6—7 kK, we obtain transition energies in agreement with the assignment of De Kock and Gruen [191]. The introduction of *d*—*p* mixing leads to a reasonable value for the parameter Δ_t in a regularly tetrahedral $CuCl_4^{2-}$ ion; the simple angular overlap model, in common with the crystal field model, leads to excessive values for this parameter if it is calculated from the parameters required to fit chlorocuprate(II) spectra. However, this refined angular overlap treatment requires four freely-chosen parameters.

(c) Semi-empirical MO calculations

Semi-empirical MO calculations, based on the extended Hückel approach, have been performed on a number of chlorocuprates(II). The earliest and simplest of these, the work of Lohr and Lipscomb [86] on the $CuCl_4^{2-}$ ion, were perhaps the most interesting; we have already noted how they found an energy minimum close to the experimentally-determined configuration of the ion in compounds such as Cs_2CuCl_4. From the spectroscopic point of view, their calculated *d*—*d* transition energies for D_{2d} $CuCl_4^{2-}$ were in good agreement with those reported later by Ferguson [165]. For square coplanar $CuCl_4^{2-}$, they found the energy sequence $b_{1g} > b_{2g} > e_g > a_{1g}$ for the ligand field orbitals, but their calculated transition energies were much too high. The same energy sequence was found by Ros and Schuit [202,203], using a more elaborate model, though their *d*—*d* transition energies were too low, in the range 6—9 kK.

A Wolfsberg—Helmholz calculation on $CuCl_5^{3-}$ [204] led to the proposal that the band at 10 kK might be of charge transfer origin, but additional evidence would be needed before such a suggestion need be taken seriously.

We should note a number of other MO calculations on chlorocuprates(II), although they did not necessarily seek to calculate *d—d* transition energies; there have been treatments of $CuCl_2$ [205], $CuCl_6^{4-}$ [154], $CuCl_4^{2-}$ [206,207], $CuCl_5^{3-}$ [65,96] and various dimeric species [155,208].

(d) Ab initio SCF calculations

The $CuCl_4^{2-}$ ion has been the subject of extensive ab initio calculations [89]. We have already noted that these led to an energy minimum for a flattened tetrahedron similar to that found in, e.g. Cs_2CuCl_4. For square coplanar $CuCl_4^{2-}$, *d—d* transition energies were calculated by determining the total energies of the $^2B_{1g}$, $^2B_{2g}$, ^2E_g and $^2A_{1g}$ states; their relative energies were found to be $^2B_{1g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$, in agreement with the assignment proposed above under (ii). The transition energies were calculated to lie in the range 7—11 kK, rather low compared with experimental data. However, the model seems to arrive at the correct relative energies and, bearing in mind the fact that these transition energies are only a small fraction of the total energy of the ion, this work must be regarded as a remarkable achievement. It remains to be seen whether this success can be repeated for other chlorocuprate(II) ions, and whether such ab initio calculations will someday render the simple empirical models obsolete as convenient tools for the interpretation of chlorocuprate(II) *d—d* spectra.

E. CHARGE TRANSFER SPECTRA

At energies upwards of 20 kK, the spectra of chlorocuprates(II) are dominated by intense charge transfer absorption; the excited states arise from filled non-bonding or weakly bonding MO's which are largely localised on the ligands, to the singly-occupied orbital of the partly-filled shell. These transitions are not easy to study in crystalline chlorocuprates(II). Their high intensities make single crystal transmission work difficult, while other techniques for measuring solid state spectra can be unreliable in the UV. The theoretical interpretation of charge transfer spectra is clearly more troublesome than for *d—d* spectra, although, in principle, the former should provide more information about bonding and electron distribution. Interest in the charge transfer spectra of chlorocuprates(II) began to develop strongly in the mid-1960's but seems to have subsided in more recent years.

(i) The $CuCl_4^{2-}$ ion

The charge transfer spectrum of the D_{2d} $CuCl_4^{2-}$ ion has been rather thoroughly studied. Published data are summarised in Table 9. The charge transfer transitions occur at about 22 (shoulder), 25, 29 (shoulder), 34 and 43 kK. Molar extinction coefficients have not been measured for work on single crystals, but the UV spectra of solutions which probably contain $CuCl_4^{2-}$ ions show these to be around 3000 l mol^{-1} cm^{-1}.

The assignment of the charge transfer spectrum of $CuCl_4^{2-}$ led to some difficulties. A qualitative MO diagram indicates three filled non-bonding MO's

TABLE 9

Charge transfer spectrum of the $CuCl_4^{2-}$ ion

Compound	E (kK)	T (K)	Method	Ref.
Cs_2CuCl_4	23.0sh, 24.8, 29.0sh, 34.0, 34.5, 42.4	77	SCP	165
	22.7sh, $\left\{\begin{matrix}24.6,\\ 24.9,\end{matrix}\right.$ $\left\{\begin{matrix}28.4\text{sh},\\ 29.3\end{matrix}\right.$ 33.1, 33.9, 43.0	77	SCP	92
$Cs_2Zn(Cu)Cl_4$	22.8sh, $\left\{\begin{matrix}24.6,\\ 24.9,\end{matrix}\right.$ $\left\{\begin{matrix}28.6,\\ 29.4\end{matrix}\right.$ 33.1, 33.8, 42.9	77	SCP	92
$(TMBA)_2CuCl_4$	22.7sh, 25.0, 29.4	298	SCP	169
$(NMe_4)_2CuCl_4$	25.0, 36.0, 43.5	298	R	166
$(Me_2NH_2)_2CuCl_4$	22.0, 34.5, 44.5	298	R	166
$(NBu_4)_2CuCl_4$	22.2sh, 25.0, 29.4sh, 31.8, 38.5	298	R	168

Notes: Transition energies bracketed together are the peak positions observed in different polarizations. TMBA = $C_6H_5CH_2N(CH_3)_3$; Bu = n-C_4H_9 (other abbreviations are as used in previous tables).

(a_2, e) largely localised on the ligands, five filled weakly π-bonding MO's (a_1, b_1, b_2, e) and four relatively strongly σ-bonding MO's (a_1, a_2, e). Transitions from $^2B_2$ to ^2E and $^2A_1$ states are electronically allowed. Thus Ferguson [165] assigned the band at 24.8 kK to the ^2E excited state arising from a hole in the non-bonding e orbital, while the shoulder at 23 kK was attributed to the forbidden transition to the $^2A_2$ state, with the hole in the a_2 non-bonding orbital. The next two bands at 29 kK and 34 kK were both assigned to $^2B_2 \rightarrow {}^2E$ transitions, arising respectively from transitions out of π- and σ-bonding MO's, while the bands at 34.5 kK and 42.4 kK were attributed to $^2B_2 \rightarrow {}^2A_1$ transitions. However, Sharnoff and Reimann [92] considered the effects of spin-orbit coupling and the distortion from D_{2d} geometry; this led to the prediction that the ^2E states should be split into two components, polarized in different directions. Such considerations produced the assignment of the band pairs observed around 25, 29 and 34 kK to $^2B_2 \rightarrow {}^2E$ transitions, contrary to Ferguson's assignment of the last of these to a $^2B_2 \rightarrow {}^2A_1$ transition. Sharnoff and Reimann agreed with Ferguson's assignment of the 43 kK band to $^2B_2 \rightarrow {}^2A_1$, but offered no assignment for the shoulder at 22.7 kK. The most elaborate analysis of transition metal tetrahalide spectra has been performed by Bird and Day [209]. They assigned the weak band around 23 kK and the stronger one at 25 kK to the $^2A_2$ and ^2E states (respectively) which arise from holes in the non-bonding a_2 and e orbitals, following Ferguson [165]. However, they prefer to assign the weak 29 kK band to the forbidden transition $^2B_2 \rightarrow {}^2B_2$, the excited state arising from a hole in the b_2 weakly π-bonding MO. Their argument was based on the Jahn—Teller splitting of the tetrahedral $^2T_2$ state into ^2E and $^2B_2$, which suggests the assignment of the 29 kK band to the $^2B_2$ component and the 34 kK band to the ^2E. Magnetic circular dichroism studies [210,211] are generally in agreement with the assignments of Bird and Day (see also Sect. H).

(ii) Tetragonal octahedral $CuCl_6$ systems

Little work has been done on the charge transfer spectra of these. Willett et al. [166] measured mull transmission spectra of $(MeNH_3)_2CuCl_4$ and $(EtNH_3)_2CuCl_4$, and reported bands at 24.0, 33.3 and 49.0 kK, with a shoulder at 38.5 kK. No assignments were proposed, but the 24 kK band may be assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2u}$ transition, where the hole in the excited state resides in the b_{2u} non-bonding orbital. The 33 kK and 49 kK bands would probably be ${}^2B_{1g} \rightarrow {}^2E_u$ transitions, involving π- and σ-bonding MO's, respectively. The shoulder at 38.5 kK must be a forbidden charge transfer band of indeterminate origin. These assignments consider only square $CuCl_4^{2-}$ species and ignore the possibility of charge transfer from long-bonded ligands.

(iii) The $CuCl_5^{3-}$ ion

The charge transfer spectrum of $CuCl_5^{3-}$ is complicated by the fact that it is stabilized by tripositive cations with *d—d* bands in the visible and near-UV. Analysis of the spectra of $[M(NH_3)_6]CuCl_5$ (M = Cr, Co, Rh, Ru) has made it possible to identify charge transfer bands at 24, 27 and 37 kK [185]. The shoulder at 24 kK may be tentatively assigned to ${}^2A_1' \rightarrow {}^2A_2''$, arising from transfer of an electron from the weakly π-bonding a_2'' MO. The two more intense bands at 27 and 37 kK presumably involve electron transfer from weakly π-bonding e' MO's.

(iv) $Cu_2Cl_6^{2-}$ dimers

The charge transfer spectra of compounds containing $Cu_2Cl_6^{2-}$ dimers (and indeed, all chlorocuprates(II) containing symmetric or nearly symmetric Cu—Cl—Cu bridges) are characterised by a band at unusually low energy, about 19 kK in almost planar dimers and 21 kK in significantly non-planar dimers as in $AsPh_4CuCl_3$ [168,212]. The band is polarized in the direction of the Cu—Cu axis. Willett and Liles [188] showed that in a planar $Cu_2Cl_6^{2-}$ ion, the orbitals on the two metal atoms which accommodate the odd electrons are combined to form two MO's, b_{2u} and b_{1g}, fairly close in energy. Thus Willett and Liles proposed that the ground state of $Cu_2Cl_6^{2-}$ is ${}^1B_{3u}$, with a ${}^3B_{3u}$ excited state lying nearby. A more elaborate analysis [208] leads to substantially similar results. We shall discuss the ground state of $Cu_2Cl_6^{2-}$ further in Sect. G, when we come to look at its magnetic properties. Transitions polarized along the Cu—Cu direction (labelled x in the notation of Willett and Liles) must arise from excited states corresponding to promotion of an electron from the non-bonding in-plane π-orbitals b_{1g} and b_{2u}. The unusually low transition energy associated with such an electron transfer from these orbitals is related to the fact that the orbitals on the bridging chlorines which might be involved in the donor MO's are also engaged in σ-bonding, contrary to the situation in $CuCl_4^{2-}$. Apart from this anomalous transition at 19 kK, the charge transfer spectra of trichlorocuprates(II) generally resemble those of comparable monomeric chromophores.

(v) Other chlorocuprates(II)

$CsCuCl_3$ exhibits the characteristic 19 kK band found in other systems with symmetric, short Cu—Cl—Cu bridges; this band is apparently responsible for the garnet-red colour of all such chlorocuprates(II) [212].

Molecular $CuCl_2$ has two charge transfer bands, at 19 and 45 kK [191]. These may be assigned to the $^2\Sigma_g^+ \to {}^2\Pi_u$ and $^2\Sigma_g^+ \to {}^2\Sigma_u$ transitions, corresponding to excitations from a weakly π-bonding MO and a strongly σ-bonding MO, respectively.

(vi) Theoretical studies

The earliest theoretical work (up to about 1964) on chlorocuprate(II) charge transfer spectra was essentially qualitative, and was concerned with predicting the number of bands to be expected, their relative positions in the spectrum and their relative intensities. The paper by Braterman [213] on the spectrum of $CuBr_4^{2-}$ is a good example of how relatively simple arguments can lead to a convincing interpretation of a charge transfer spectrum. Later, it was realised that some more quantitative MO theory was needed to tackle charge transfer bands. The simple angular overlap model has been applied with some limited success [198,214]. The relative energies of the ligand orbitals can be computed in much the same way as those of the metal orbitals. The difference in energy between a non-bonding *d*-orbital and a non-bonding ligand orbital can be left as a freely chosen parameter to be fitted to experimental data, or it can be otherwise estimated. Such calculations [198, 214] have been able to fit some features of chlorocuprate(II) charge transfer spectra fairly well, but the angular overlap model is a good deal less convincing in such applications.

Semi-empirical extended Hückel calculations have been used to calculate charge transfer transition energies in chlorocuprates(II) (with the usual assumption that two-electron terms need not be considered) but with little success. For square coplanar $CuCl_4^{2-}$, Ros and Schuit [202,203] predicted the $^2B_{1g} \to {}^2B_{2u}$ transition to lie at 7.6 kK, amongst the *d—d* bands. In $CuCl_5^{3-}$ [204], the lowest-energy charge transfer bands are likewise calculated to appear in the near-IR. Since such calculations are not particularly reliable for predicting *d—d* transition energies, it is not very likely that they can tackle charge transfer spectra with any success. However, the ab initio calculation on D_{4h} $CuCl_4^{2-}$ at least managed to place the charge transfer states higher in energy than the *d—d* states [89].

The intensities of the charge transfer bands in T_d $CuCl_4^{2-}$ have been disussed theoretically [215] and the results compared with experimental data or the D_{2d} ion; the eigenvectors of Ros and Schuit [202,203] were used in e calculation. It was argued that the distortion from T_d to D_{2d} should not ffect the oscillator strengths much, and the calculated relative intensities of e bands are in good agreement with experiment, although the absolute vales of the oscillator strengths are too high by a factor of about 2.

ii) Structural diagnosis using charge transfer spectra

Charge transfer spectra are of little value for routine, preliminary structural iagnosis. The spectra do not differ drastically from one geometry to another nd the experimental difficulties involved in their accurate measurement may itroduce problems. Moreover, charge transfer spectra are more difficult to iscuss theoretically in relation to the coordination geometry of the metal. s an example of the pitfalls, consider $(dienH_3)CuCl_5$ and $[Co(NH_3)_6]CuCl_5$. hese compounds have such similar charge transfer spectra that one might e excused for supposing that the coordination geometry about the metal as the same. $(dienH_3)CuCl_5$ would be identified as containing $CuCl_5^{3-}$ ions, ather than polymeric layers $(CuCl_4^{2-})_n$ with lattice chlorides, if we were in he habit of using such spectra for structural characterisation; its charge ransfer spectrum is quite unlike that of, for example, $(MeNH_3)_2CuCl_4$. An nportant exception, however, is the 19 kK band found in chlorocuprates(II) ontaining short, symmetric Cu—Cl—Cu bridges, which seems to afford a ather reliable test for such links; the energy of this band seems to increase ith distortion of the $Cu_2Cl_6^{2-}$ dimer from planarity.

VIBRATIONAL SPECTRA

Here we are concerned only with vibrations of the anions in chlorocupratesI). Cu—Cl vibrational modes occur in the far-IR, usually below 300 cm^{-1}, a egion whose exploration was difficult until about 1960. Raman spectroscopy as impracticable for such highly-coloured species until the development of ser techniques in the mid-1960's. Despite remarkable developments in the xperimental technique of vibrational spectroscopy since then, chlorocurates(II) still pose some problems. In most cases, fewer bands are observed han might be predicted, and assignments are often far from certain. Vibraional spectroscopy can be highly misleading as a tool for routine structural iagnosis. For example, the spectra of $[Cr(NH_3)_6]CuCl_5$ [216] were difficult o interpret in terms of a D_{3h} anion, and it was suggested, prior to the definive X-ray analysis, that it might contain D_{2d} $CuCl_4^{2-}$ ions. Conversely, Booran et al. [217] were content to assign the vibrational spectra of $(dienH_3)$uCl$_5$ in terms of a trigonal bipyramidal anion, although this compound ctually contains tetragonal octahedral $CuCl_6$ chromophores. Further work needed to resolve these difficulties. However, vibrational spectroscopy has a bright future for the study of temperature- and pressure-induced phase transitions in chlorocuprates(II).

(i) The tetrachlorocuprate(II) ion $CuCl_4^{2-}$

The vibrational spectra of compounds containing discrete $CuCl_4^{2-}$ ions are summarised in Table 10. Bands below 100 cm^{-1} are not included; these are almost certainly lattice modes. Cu—Cl stretching frequencies are expected to be in the range 250—300 cm^{-1}, with bending frequencies around 100—150 cm^{-1}. An isolated D_{2d} $CuCl_4^{2-}$ ion has four stretching modes, $a_1 + b_2 + e$, and five bending modes, $a_1 + b_1 + b_2 + e$. Thus in the IR we expect to see two bands around 250 cm^{-1} and two around 150 cm^{-1}. In a T_d ion, there would be only one stretching mode and one bending mode, of t_2 symmetry; any observed splitting of these reflects the distortion from T_d to D_{2d}. In the Raman, there should be three stretching modes around 250 cm^{-1} and four around 150 cm^{-1}. A glance at the data in Table 10 shows that few of the spectra can be simply interpreted on this basis; in particular, the single crystal data show many more bands than are predicted for an isolated anion. Evidently site-group and factor-group splittings must be taken into account in dealing with these highly-resolved spectra. If such splittings are large, they may have to be considered in poorly-resolved spectra as well. The most complete spectra have been observed for Cs_2CuCl_4 and $(NMe_4)_2CuCl_4$; these will now be discussed in detail.

In $(NMe_4)_2CuCl_4$, the site group is C_s and the space group is Pnma ($D_{2h}{}^{16}$) with $z = 4$. Factor group analysis [223] leads to 36 modes, of which $6b_{1u} + 3b_{2u} + 6b_{3u}$ are allowed in the IR and $6a_g + 3b_{1g} + 6b_{2g} + 3b_{3g}$ in the Raman. Polarized IR reflectance studies [223] have identified 13 of the 15 predicted bands at 105 K; only 9 are seen at room temperature. The b_{2u} mode arising from the e stretch of the isolated ion is split into two components, separated by 5 cm^{-1}. This could be explained in a number of ways; Dunsmuir and Lane [223] suggest small rotational displacements of the anions, with the removal of some mirror planes. The fact that the isolated-ion e stretch is split overall into components covering a range of 12 cm^{-1} suggests that factor group splittings could be important in the interpretation of room-temperature data under low resolution. Dunsmuir and Lane [223] relate the bands around 290 cm^{-1} to the isolated-ion e stretch, the bands at ca. 230 cm^{-1} to the b_2 stretch, and the lower-energy bands to the e and b_2 bending modes, with the latter being higher in energy.

Cs_2CuCl_4 also has the space group Pnma (or Pnam) ($D_{2h}{}^{16}$). Less complete IR reflectance data are available; two peaks at 296 cm^{-1} and 288 cm^{-1} are ascribed to the isolated-ion e stretching mode, with the b_2 stretch at 258 cm^{-1}, the b_2 bend at 151 cm^{-1} and the e bend at 136 and 121 cm^{-1}. It may be noted that the separation of the e and b_2 stretches is rather less than for $Cs\,CuCl_4$, and this has been related [19] to the degree of flattening of the tetrahedron, using old crystallographic data [175]. However, the latest X-ray

TABLE 10

Vibrational spectra of $CuCl_4^{2-}$ ions

Compound	ν (cm^{-1})	T (K)	Technique	Ref.
Cs_2CuCl_4	292, 257	298	IR	216
	288, 256	298	IR	218
	288, 255	298	IR	219
	292, 265, 260, 149, 126	298	IR	19
	296, 288, 258, 151, 136, 123	298	IRC	19
	295, 265	298	IR	221
	295, 250	298	R	219
	299, 253, 140, 121, 106	298	R	220
	297, 280, 256, 253, 251, 149, 141, 136, 126, 120, 105, 103	298	RC	220
$(NMe_4)_2CuCl_4$	281, 237, 145, 128	298	IR	222
	278, 236	298	IR	216
	285, 283, 278, 275, 272, 234, 145, 130, 127, 126	298	IRC	223
	300, 295, 292, 288, 283, 279, 239, 238, 155, 151, 136, 134, 130, 118	105	IRC	223
	276, 232	298	R	219
$(NEt_4)_2CuCl_4$	298, 268, 247	298	IR	218
	267, 248, 136, 118	298	IR	222
	267	298	IR	39
	275	298	IR	221
	277	298	R	219
$(Ph_3MeAs)_2CuCl_4$	283	298	IR	218
$(Me_2NH_2)_3CuCl_5$	295, 230, 130	298	IR	147
(imidazolium)$_2$$CuCl_4$	290, 228	298	IR	224
	286, 242, 185	298	R	224
$(Me_2CHNH_3)_2CuCl_4$	290, 232	343	IR	152
	301, 279, 181	298	IR	152
	295, 281, 193	298 [a]	IR	152
	301, 271, 181	78	IR	152
	301, 275, 189	78 [b]	IR	152
	290	343 [b]	IR	152
$(Et_2NH_2)_2CuCl_4$	287, 282, 186	298	IR	152
	295, 220	343	IR	152
$(C_9H_7S_2)_2CuCl_4$	285, 272, 235	298	IR	33
Cs_3CuCl_5	288, 271, 225, 132, 120	298	IR	19
$(PPh_4)_2CuCl_4$	330, 310, 260	298	IR	221
$(AsPh_4)_2CuCl_4$	330, 308, 262	298	IR	221
(24DMBD)$_2$$CuCl_4$	305, 260	298	IR	172
(248TMBD)$_2$$CuCl_4$	281	298	IR	172
(2478TMBD)$_2$$CuCl_4$	308, 258	298	IR	172

[a] Under 20 kbar pressure.

[b] Under 12 kbar pressure.

IR = infrared, R = Raman, C = single crystal measurement (other abbreviations are as used in previous tables).

structures [65,66] show that the tetrahedra in these two compounds are about equally flattened.

In the single crystal Raman spectrum of Cs_2CuCl_4, 12 of the 18 expected bands are observed [220], and were assigned as follows: 297, 280 (a_1 stretch); 256, 253, 251 (e stretch); 149, 141, 136 (e bend); 126, 120 (b_2 bend); 105 (b_1 bend) and 103 (a_1 bend). There is cause for disquiet in that this spectrum places the a_1 stretch at higher energy than the e stretch, whereas the reverse is apparently the case in $(NMe_4)_2CuCl_4$ [223]. The relative energies of the b_2 and e bending modes are likewise reversed. This is curious, since the anions are of almost identical geometry in these two systems. Discrepancies such as this in the interpretation of well-resolved, single crystal data do not auger well for the application of vibrational spectroscopy to structure determination in chlorocuprates(II).

McGinnety [65] has performed a normal coordinate analysis for Cs_2CuCl_4, using the assignments of Beattie et al. [220] except that the band at 136 cm^{-1} was reassigned to the b_1 bending mode. A stretching force constant of 1.08 mdyn Å rad^{-2} was obtained, together with bending force constants of 0.37 and 0.59 mdyn Å rad^{-2} (the larger referring to the smaller Cl—Cu—Cl angle), and interaction force constants of 0.43 and 0.17 mdyn Å rad^{-2}. The stretching force constant was in good agreement with the value of 1.13 mdyn Å rad^{-2} which gave the best fit to McGinnety's calculations of crystal forces [65].

The vibrational spectrum of the discrete, square coplanar $CuCl_4^{2-}$ ion has yet to be analysed in detail, although some of the results for tetragonal $CuCl_6$ systems (discussed below) are clearly relevant. As we distort from D_{2d} to D_{4h}, the b_2 stretching mode of the D_{2d} ion becomes an a_{2u} bending mode of the D_{4h} ion, and should therefore decrease in energy as the tetrahedron is flattened towards square coplanarity. In the high-temperature phase of $(Me_2CHNH_3)_2CuCl_4$, which apparently contains only D_{2d} ions, the b_2 stretch is seen at 232 cm^{-1} [152]. At room temperature and under 20 kbar pressure, this moves to 193 cm^{-1}, indicating square coplanar anions in the high-pressure phase. In $(Et_2NH_2)_2CuCl_4$ at room temperature, a band is observed at 186 cm^{-1}; this shifts to 220 cm^{-1} in the high-temperature phase, indicating a transition from square coplanar to flattened tetrahedral geometry. Studies of this kind, complemented by electronic spectral measurements, promise to be of great value in the study of phase transitions in chlorocuprates(II).

(ii) Compounds containing tetragonal octahedral $CuCl_6$ chromophores

To a first approximation, the vibrational spectra of $(RNH_3)_2CuCl_4$ systems may be assigned on the basis of a square coplanar $CuCl_4^{2-}$ ion, perhaps with some distortion to D_{2h}. Published spectra are listed in Table 11. In the IR, we expect a single e_u stretching mode around 300 cm^{-1}, e_u and a_{2u} bending modes being predicted to lie at lower energy. In the Raman, we expect an intense a_{1g} stretch at about 300 cm^{-1}, a weaker b_{1g} stretch, and, at lower energy, e_g and b_{2g} bending modes. The spectra in Table 11 cannot be readily interpreted on

TABLE 11

Vibrational spectra of compounds containing tetragonal octahedral $CuCl_6$ chromophores

Compound	ν (cm^{-1})	T (K)	Technique	Ref.
$(NH_4)_2CuCl_4$	297, 247, 235, 185	298	R	220
$(MeNH_3)_2CuCl_4$	296, 218, 164, 149, 121, 110, 101	1.2	IR	225
	284	298	IR	216
	285, 247, 181	298	R	220
$(EtNH_3)_2CuCl_4$	286, 248, 202, 182, 174 133, 114	298	RC	220
	279	298	IR	216
	294, 278, 182	298	IR	152
	304, 238, 169, 144, 119, 110, 100	1.2	IR	225
$(n\text{-}C_3H_7NH_3)_2CuCl_4$	296, 248, 169, 144, 118, 109	1.2	IR	225
$(n\text{-}C_4H_9NH_3)_2CuCl_4$	280, 211, 174, 148, 118, 101	1.2	IR	225

this basis, and factor group analysis is required, at least for the single crystal and low temperature data. Beattie et al. [220] have discussed the correlations between the isolated-ion modes in $(MeNH_3)_2CuCl_4$ with the site symmetry $D_{4h}{}^5$, the site factor group $D_{2h}{}^9$ and the structure factor group $D_{2h}{}^{18}$. This analysis leads to the assignment of the Raman bands at 247 and 181 cm^{-1} as arising from the isolated-ion a_{1g} and b_{1g} stretches, and the bands can be described respectively as vibrations involving terminal and bridging Cl atoms. The bands at 285 and 174 cm^{-1} are derived from the same a_{1g} and b_{1g} isolated-ion stretches, coupled out of phase. The low-temperature IR spectra have not been assigned in detail; Stoelinga and Wyder [225] give the structure factor group as C_{2h}.

The question of Cu—Cl stretching frequencies involving long-bonded chlorines is clearly a matter of some interest. For the $(RNH_3)_2CuCl_4$ systems, we cannot unambiguously identify such frequencies since the bands at 174 and 182 cm^{-1} involve simultaneous contraction of a long bond and elongation of a short bond (and vice versa). In the Raman spectrum of $CuCl_2 \cdot 2H_2O$ [220] a band at 112 cm^{-1} might be attributed to a long Cu—Cl stretch; the structure [227] contains *trans*-$[CuCl_2(H_2O)_2]$ planar molecules, which form infinite chains by formation of long Cu—Cl links. The band at 112 cm^{-1} is best regarded as a libration of linear Cl—Cu—Cl chains in different molecules with one another. $K_2CuCl_4 \cdot 2H_2O$ contains [227] *trans*-$[CuCl_4(H_2O)_2]^{2-}$ anions with two short and two long Cu—Cl bonds. Bands at about 140 cm^{-1} are associated with motion of the long-bonded Cl atoms, and have been regarded as ionic lattice modes [228]. The short Cu—Cl bond stretch is found in the Raman at 228 cm^{-1} [228].

(iii) The $CuCl_5^{3-}$ ion

The vibrational spectrum of $CuCl_5^{3-}$ has yet to be observed in its entirety. Published data are given in Table 12. In the IR, we expect an a_2'' mode arising from the antisymmetric stretching of the axial bonds and an e' mode arising from the equatorial bond stretches. Since the axial bonds are appreciably shorter, we might expect the a_2'' mode to appear at higher energy. In the Raman, there should be two intense a_1' symmetric stretching frequencies which may be strongly coupled, and an e' stretch which should be coincident with that predicted in the IR. In addition, of course, we can predict various bending modes, but very few bands have been seen below 200 cm^{-1} in pentachlorocuprates(II) containing the $CuCl_5^{3-}$ ion, and, as will be seen, the Cu—Cl stretching region presents enough problems by itself.

The intense band observed in the Raman at 260 cm^{-1} may be assigned to one of the a_1' symmetric stretches, but the position of the other is uncertain. The band in the IR at about 270 cm^{-1} could be either a_2'' or e'; Long et al. [120] favour the former assignment, since they found no coincident band in the Raman. However, Boorman et al. [217] saw shoulders at 275 and 285 cm^{-1} in the Co and Cr salts, respectively. Only Day [229] has observed a second IR band in the high-frequency region, a shoulder at 254 cm^{-1}; this could well be the a_2'' stretch. The lower-frequency region is somewhat con-

TABLE 12

Vibrational spectra of $CuCl_5^{3-}$ ions: all measurements made at room temperature

Compound	ν (cm^{-1})	Technique	Ref.
$[Cr(NH_3)_6]CuCl_5$	268	IR	216
	270	IR	185
	280, 200, 180, 142	IR	217
	285, 250	R	217
$[Co(NH_3)_6]CuCl_5$	269	IR	216
	273	IR	185
	267, 254	IR	229
	270, 200, 180, 150	IR	217
	268	IR	120
	275, 255, 240, 200, 180	R	217
	260, 170	R	120
$[Co(NH_3)_5H_2O]CuCl_5$	256	IR	120
	262, 175	R	120
$[Rh(NH_3)_6]CuCl_5$	274	IR	185
$[Ru(NH_3)_6]CuCl_5$	267	IR	185

TABLE 13

Vibrational spectra of $Cu_2Cl_6^{2-}$ dimers

Compound	ν(cm^{-1})	T (K)	Technique	Ref.
NH_4CuCl_3	311, 280, 230	298	IR	216
	309, 283	298	IR	230
	305, 280	17	IR	230
$KCuCl_3$	301, 278, 230, 193	298	IR	216
$PhCH_2CH_2NMeH_2CuCl_3$	290, 275	298	IR	134

fusing. Boorman et al. [217] observed a moderately strong Raman band at 200 cm^{-1}, but Long et al. did not [120]. The assignment of the bending modes must await further work. It should be pointed out that cation vibrations can be troublesome in pentachlorocuprates(II), and Boorman et al. [217] admit that their spectra are poorly-resolved. All workers report broad bands, with half-widths of about 30 cm^{-1}. Low-temperature measurements are needed before we can assign the bands reliably. Unfortunately, the cubic structures of these compounds prevents the use of polarization data.

(iv) $Cu_2Cl_6^{2-}$ dimers

Relatively little work has been done on the vibrational spectra of trichlorocuprates(II) containing $Cu_2Cl_6^{2-}$ dimers. Published data are summarised in Table 13. The bands around 300 cm^{-1} are attributed to terminal Cu—Cl stretches, while the bands at 280 and 230 cm^{-1} are probably stretching frequencies involving bridging chlorines. Heyns and Schutte [230] were mainly concerned with the vibrations of the cation in NH_4CuCl_3; these revealed a phase change between 85 and 45 K. A transition to an antiferromagnetic state is proposed around 45 K. The band seen at 193 cm^{-1} in $KCuCl_3$ is likely to be a bending mode involving terminal chlorines, although it is possible that the 230 cm^{-1} and 193 cm^{-1} bands are both essentially stretching frequencies involving bridging chlorines.

(v) $CsCuCl_3$

The interpretation of the vibrational spectrum of $CsCuCl_3$ clearly demands line-group or factor-group analysis. Published spectra are summarised in Table 14. The appropriate factor group is D_6^2, and the well-resolved spectra have been assigned accordingly. The observed vibrations can be classified as involving terminal Cl atoms (Cu—Cl$_t$, 2.281 Å) or bridging Cl atoms (Cu—Cl$_b$, 2.355 Å). Vibrations associated with the long (2.776 Å) Cu—Cl bonds were considered to lie at much lower energies. Thus the highest-frequency bands at 304, 295 and 287 cm^{-1} were assigned to Cu—Cl$_t$ stretches, and the lower-

TABLE 14

Vibrational spectra of $CsCuCl_3$

ν (cm^{-1})		T (K)	Technique	Ref.
(xy)	287, 256, 193, 166, 150, 135	80	IRC	231
(z)	304, 261, 181, 140			
	288, 260, 188, 180, 172, 158, 145, 111	298	IR	232
	293, 287, 263	298	IR	216
	295, 271, 252, 199, 193, 182, 166, 139, 116, 111	80	RC	231

frequency bands at 271, 261, 256 and 252 cm^{-1} to Cu—Cl_b stretches. The bands below 200 cm^{-1} were assigned to bending modes, with those involving the shorter terminal Cl atoms at higher frequency than those involving bridging chlorines

G. MAGNETIC AND ESR STUDIES

Transition metal chemists have traditionally measured the magnetic susceptibilities of bulk material over a limited temperature range, and converted the results into effective paramagnetic moments μ_{eff}. Such measurements on chlorocuprates(II) have produced the results that would be expected from the application of elementary theory: the Curie—Weiss law is usually obeyed rather well, at least down to about 77 K, and μ_{eff} values of around 1.9 B.M. are obtained, as expected for a d^9 system with a small positive orbital contribution arising from spin-orbit coupling. Much more interesting behaviour is often encountered at lower temperatures, where ferromagnetic and antiferromagnetic interactions may manifest themselves. ESR measurements provide complementary information about the anisotropic g-tensor, and, in principle, should reveal much about the electron distribution and bonding. The most important magnetic work on chlorocuprates(II) concerns the anisotropic behaviour of discrete ions like $CuCl_4^{2-}$, and magnetic exchange interactions between copper atoms in dimeric and polymeric anions.

(i) Compounds containing discrete $CuCl_4^{2-}$ ions

Interest in the $CuCl_4^{2-}$ ion has been focussed upon its magnetic anisotropy (a necessary consequence of D_{2d} geometry). The principal components of the anisotropic g-tensor, assuming that spin-orbit coupling is small compared with the tetragonal component in the ligand field, may be expressed as

$$g_{xx} = g_{yy}\ (= g_\perp) = 2.0023(1 - \lambda/E_1)$$

$$g_{zz}\ (= g_{\parallel}) = 2.0023(1 - 4\lambda/E_2)$$

$$g_{av} = (2g_{\perp} + g_{\parallel})/3 = 2.0023(1 - 2\lambda/3E_1 - 4\lambda/3E_2)$$

where λ is the spin-orbit coupling constant (—0.83 kK for a free Cu^{2+} ion), E_1 is the difference in energy between the $^2B_2$ and ^2E ligand field states, and E_2 is the difference in energy between the $^2B_2$ and $^2B_1$ states. The effects of covalency may be taken into account by introducing the factors $k_{\parallel}$ and $k_{\perp}$ in the terms involving λ [233]. Any distortion from D_{2d} (e.g. to C_s) will be reflected in a splitting of $g_{\perp}$. More complete expressions for the g-values, in terms of MO mixing coefficients and including spin-orbit mixing of charge transfer states into the ground state, have been given [234]. The ESR spectrum measures these g-values directly, and published data are given in Table 15. These g-values should be strongly dependent on the degree of tetragonal distortion from T_d, since the d—d transition energies E_1 and E_2 increase sharply with the flattening angle θ. In copper-doped K_2PdCl_4 we may reasonably expect to be looking at square coplanar $CuCl_4^{2-}$ ions, and $(Et_2NH_2)_2CuCl_4$ in its room-temperature phase is believed to contain discrete $CuCl_4^{2-}$ ions which are square coplanar, or nearly so [147,152]. As expected, the g-values for these are much lower than those found in less flattened $CuCl_4^{2-}$ tetrahedra.

ESR data also yield hyperfine and superhyperfine coupling constants, which can lead to useful information about the compositions of the highest-energy molecular orbitals. In Cs_2CuCl_4, Sharnoff [91] failed to resolve the superhyperfine structure but was able to set a lower limit on the bandwidths. In conjunction with hyperfine data and g-values, Sharnoff deduced that the unpaired electron spent 18% of its time on the ligand atoms. An important feature of Sharnoff's treatment was the explicit consideration of $3d$—$4p$ mixing; the unpaired electron apparently spends 12% of its time in a copper $4p$-orbital.

The most detailed ESR study of a $CuCl_4^{2-}$ ion was performed on copper-doped K_2PdCl_4, which is deemed to contain square coplanar anions. Spin-

TABLE 15

ESR g-values for $CuCl_4^{2-}$ ions

Compound	$g_{\perp}$	$g_{\parallel}$	g_{av}	T (K)	Method	Ref.
Cs_2CuCl_4	2.083 2.105	2.384	2.191	77	C	91
$Cs_2Zn(Cu)Cl_4$	2.083 2.101	2.446	2.210	77	C	91
$K_2Pd(Cu)Cl_4$	2.049	2.2326	2.110	77	C	235
$(Et_2NH_2)_2CuCl_4$	2.050	2.253	2.118	298	P	149
	—	—	2.159	338	P	149

C = single crystal measurement; P = polycrystalline powder measurement.

Hamiltonian parameters were determined and analysed in terms of the most complete expressions for the g-values, in terms of MO coefficients and electronic excited state energies [233,235]. Mixing coefficients for the b_{1g}, b_{2g} and e_g ligand field orbitals giving the best fit to the expressions for the spin-Hamiltonian parameters were obtained. Unfortunately, electronic spectroscopic data for tetragonal octahedral $CuCl_6$ chromophores were used in the analysis: the d—d spectrum of square coplanar $CuCl_4^{2-}$ is now known to be rather different from that of the tetragonal $CuCl_6$ chromophore, although the $^2B_{2g}$ and ^2E_g states are apparently less affected by complete removal of the long-bonded axial ligands than the $^2A_{1g}$ state (as would be expected by conventional ligand field analysis) and the error induced by this procedure may not be too serious. As we shall see, the ESR spectrum of square coplanar $CuCl_4^{2-}$ is not greatly affected by the approach of distant axial ligands.

The anisotropic magnetic susceptibility of the D_{2d} $CuCl_4^{2-}$ ion has attracted considerable interest. The observation that $K_{\parallel}$ was greater than $K_{\perp}$ evoked some surprise, since it was expected that the orbital contribution would be more quenched when the field was parallel to the S_4 axis; in other words, the proximity of the ^2E state to the $^2B_2$ ground state should ensure that $g_{\perp} > g_{\parallel}$. This, of course, is not the case, as can be seen from the ESR data in Table 15. The 'anomalous' anisotropy was attributed to the anisotropy of the orbital reduction factor k [236—238], but this is not so great as to be entirely responsible. The problem arises from the neglect in simple treatments [239] of the $^2A_1$ and $^2B_1$ states in the basis set. Spin-orbit mixing of $^2B_1$ into $^2B_2$ increases $g_{\parallel}$ and leads to higher values of $K_{\parallel}$. It may be argued that this is a trivial result, looking at the expressions for the g-values given above. But remember that magnetochemists would like to be able to cope with systems with only a very small distortion from T_d geometry, where these expressions fail; obviously, $g_{\perp}$ cannot tend to infinity as E_1 vanishes, and the calculation of magnetic susceptibilities from the Van Vleck equation depends on other considerations besides g-factors. The most elaborate treatment [240,241] takes a basis set of all the d—d states under the simultaneous perturbation of the tetragonal crystal field and spin-orbit coupling. The resulting wave functions are then perturbed by the magnetic field operator and the resulting matrix elements substituted into the Van Vleck equation. This leads to the correct sign of the anisotropy for $CuCl_4^{2-}$ ions where the tetragonal distortion is sufficient to split the tetrahedral $^2T_2$ ground state by about 3 kK. For smaller distortions, $K_{\perp}$ should be greater than $K_{\parallel}$.

Bulk susceptibility data, translated into effective magnetic moments μ_{eff}, are much less illuminating than single crystal anisotropy data; however, a recent report [242] claims a correlation between μ_{eff} and the flattening angle θ of the $CuCl_4^{2-}$ ion. This is not surprising, since the g-values are expected to decrease with flattening. Most tetrachlorocuprates(II) containing discrete $CuCl_4^{2-}$ ions have μ_{eff} values of 1.9—2.0 B.M.; the theory of Figgis and Harris [239] predicts that a regularly tetrahedral $CuCl_4^{2-}$ ion should have an effective magnetic moment of about 2.2 B.M.

(ii) Tetragonal octahedral $CuCl_6$ chromophores

The layer compounds $(RNH_3)_2CuCl_4$ have aroused much interest as examples of two-dimensional $S = \frac{1}{2}$ Heisenberg ferromagnets [243,244]. Susceptibility measurements at relatively high temperatures lead to 'normal' magnetic moments of about 1.9 B.M. At low temperatures (below about 50 K) the Curie—Weiss law is no longer obeyed, and the susceptibility becomes field-dependent. The rather detailed magnetic studies on these compounds can be interpreted in terms of a ferromagnetic exchange interaction between copper atoms within the layers, with a much weaker antiferromagnetic exchange between copper atoms in different layers. Above a transition temperature of about 10 K, the compounds behave as two-dimensional ferromagnets; at lower temperatures, they are regarded as a special class of three-dimensional antiferromagnets. The exchange coupling constant J for the ferromagnetic intra-layer interaction is about 10 cm^{-1}; the corresponding constant J' for the antiferromagnetic inter-layer interaction is about three orders of magnitude smaller, and depends on the separation between the layers. This is largely controlled by the size of the cation; for straight-chain alkylammonium cations, the interlayer separation increases by about 1.5 Å per CH_2 added to the chain. Most of this work is probably of more interest to solid-state physicists than to coordination chemists, and we shall be content to conclude this discussion with a list of references [105,243—259].

ESR spectra of these tetragonal systems produce typical g-values of $g_\perp$ = 2.05 and $g_\parallel$ = 2.25, comparable with those found for square coplanar $CuCl_4^{2-}$; evidently the distant axial ligands have little effect, as predicted by theory [234]. Published data are summarised in Table 16.

(iii) Pentachlorocuprates(II) containing discrete $CuCl_5^{3-}$ ions

An early study of $[Co(NH_3)_6]CuCl_5$ reported [106] that the compound obeyed the Curie—Weiss law between 2 and 4 K, with μ_{eff} = 1.47 B.M., while measurements in the range 77—300 K lead to μ_{eff} = 1.85 B.M. A later study

TABLE 16

ESR g-values for compounds containing tetragonal octahedral $CuCl_6$ chromophores (all data obtained from single crystals)

Compound	$g_\parallel$	$g_\perp$	Ref.
$(MeNH_3)_2CuCl_4$	2.238	2.046	166
	2.274	2.054	184
	2.281	2.056	260
$(EtNH_3)_2CuCl_4$	2.230	2.044	166
	2.276	2.054	260

was performed [261] over the temperature range 2—38 K; Curie—Weiss behaviour was found between 16 K and 38 K, with $\theta = 17$ K and μ_{eff} 1.95 B.M., in agreement with the theory for a $^2A_1'$ ground state [262]. An antiferromagnetic transition was found near 8 K; the coupling mechanism is presumably of the 'cation—anion—anion—cation' variety [263].

The only magnetic study of $[Cr(NH_3)_6]CuCl_5$ covers, unfortunately, only the restricted temperature range of 77—305 K [264]. The Curie—Weiss law was obeyed, with $\theta = 11$ K and $\mu_{eff} = 4.34$ B.M. Estimating μ_{eff} for the cation to be 3.9 B.M., μ_{eff} for the anion is about 1.85 B.M. Thus the magnetic properties of the Cr and Co salts are much the same above 77 K. There is no evidence for any interaction between the cation and the anion in the Cr compound, although measurements at much lower temperatures would be needed to settle the point.

The ESR spectrum of the Co salt [181] yields $g_{av} = 2.157$. For an $^2A_1'$ ground state, $g_\parallel$ should be equal to 2.0023, with $g_\perp = 2.0023(1 - 3\lambda/\Delta)$, where Δ is the energy of the $^2E''$ state relative to the ground state. Hence $g_\perp$ is about 2.234. Note that measurements of g_{av} do not provide a diagnostic test for stereochemistry; g_{av} values for $CuCl_4^{2-}$ ions range from 2.1—2.2, depending on the degree of flattening of the tetrahedron, and a g_{av} of 2.16 could be equally consistent with a $CuCl_5^{3-}$ ion or with a highly-flattened $CuCl_4^{2-}$ ion.

(iv) Compounds containing $Cu_2Cl_6^{2-}$ dimers

Interest here is focussed upon magnetic interactions between the chlorine-bridged copper atoms within the dimer, although in polymerised systems like $KCuCl_3$ inter-dimer interactions may warrant consideration. Willett and Liles [188] discussed how the two highest-energy MO's in planar $Cu_2Cl_6^{2-}$, labelled b_{1g} and b_{2u} in D_{2h} symmetry, would accommodate two electrons, and how either a triplet or a singlet ground state was possible, with (respectively) a low-lying singlet or triplet excited state. Magnetic measurements on $KCuCl_3$ were performed down to liquid helium temperature [265]. Above 17 K, the data were consistent with a singlet ground state; the susceptibility begins to decrease below 32 K as the triplet excited state becomes appreciably depopulated. However, below 17.5 K the susceptibility begins to increase sharply, indicating ferromagnetic ordering. However, ESR and NQR measurements support a triplet ground state for $KCuCl_3$ [266]. The NQR evidence will be further discussed in Sect. H. The ESR signal increased in intensity on cooling from room temperature to 77 K, and persisted at a temperature as low as 1.35 K. The NQR data showed no magnetic ordering above 1.3 K, contrary to the susceptibility measurements [265].

These papers assume that $KCuCl_3$ can be treated in terms of localised dimers; we are really dealing with infinite chains, formed by the stacking of the dimers (Fig. 6). Magnetic interaction along the chain (between Cu atoms in different dimers as well as in the same dimer), and possibly also interchain interactions, need to be considered. Hara et al. [267] obtained susceptibility data similar to those of Maass et al. [265] and applied various theoretical models for magnetic interactions in chain structures. They concluded that the susceptibility data for $KCuCl_3$ could be adequately fitted on the assumption of inter-dimer exchange integrals about 0.05—0.2 times as great as those for intra-dimer interaction; both exchange integrals had negative signs, indicating a singlet ground state arising from antiferromagnetic coupling of the unpaired spins.

In $Me_2NH_2CuCl_3$, where inter-dimer interaction is likely to be weaker (see Fig. 4), Curie—Weiss behaviour is observed down to about 10 K [268]; below 10 K the susceptibility falls markedly. The data above 10 K could be equally well interpreted in terms of the Ising model for magnetic interactions in chains with $S = 1$ and $g = 1.84$, or with $S = 1/2$ and $g = 2.12$; the latter g-value is more realistic. Various other models were tried, but none was markedly more successful than another though the authors tended to favour an Ising chain of interacting dimers with singlet ground states. It is surely significant that $Me_2NH_2CuCl_3$ reaches a susceptibility maximum at a much lower temperature than $KCuCl_3$. The compounds differ structurally in that the dimethylammonium salt has weaker inter-dimer bonding, and the dimers are significantly distorted from planarity.

Magnetic and ESR measurements on $AsPh_4CuCl_3$ [269,270] confirm that the ground state of the isolated, nonplanar dimers is a spin triplet, with a singlet excited state lying some 46 cm^{-1} above the ground state. The three compounds $KCuCl_3$, $Me_2NH_2CuCl_3$ and $AsPh_4CuCl_3$ have exchange integrals $2J$ of -39, -3 and 46 cm^{-1} respectively, showing a trend from antiferromagnetic to ferromagnetic behaviour. The inter-dimer interaction diminishes along this series of compounds, and it is tempting to suggest that trichlorocuprates(II) have a ferromagnetic intra-dimer interaction, upon which is superimposed an antiferromagnetic inter-dimer exchange. However, there is recent theoretical evidence for the importance of the distortion from planarity of the dimer. If the two highest-energy occupied MO's are degenerate, a triplet ground state is expected (i.e. ferromagnetic exchange); it can be shown [208] that the singlet state is stabilized relative to the triplet by an amount proportional to the square of the energy difference between the two orbitals concerned. Extended Hückel calculations showed that in a planar $Cu_2Cl_6^{2-}$ dimer, the two orbitals are degenerate if the bridging Cu—Cl—Cu angle is 90°, but there is a significant splitting as this angle is increased; this angle is usually about 95° in $Cu_2Cl_6^{2-}$ ions. However, as the dimer is distorted from planarity at a constant bridging angle of 95°, the two highest-energy orbitals cross over with a twist angle between the planes of about 35°. Thus it is argued that in $AsPh_4CuCl_3$ (where the twist angle is 48°) the two orbitals are sufficiently close in energy that a triplet ground state is preferred, while in $KCuCl_3$, where the dimers are essentially planar, they are split by an amount large enough to stabilize the singlet ground state. This analysis is attractive, but it takes no account of inter-dimer interactions, and discrepancies in the description of the ground state of $KCuCl_3$ [265,266] have yet to be cleared up.

Few detailed measurements of ESR spin-Hamiltonian parameters have been made for trichlorocuprates(II). Powder ESR measurements on $KCuCl_3$ [265,266] agreed on an average g-value of 2.16, which seems surprisingly high for what is essentially a tetragonal octahedral $CuCl_6$ chromophore. This has been superseded by single crystal measurements [269] which give g_{xx} = 2.057, g_{yy} = 2.08 and g_{zz} = 2.215, leading to g_{av} = 2.117. An average g-value of 2.11 was found for $Me_2NH_2CuCl_3$ [268]. $AsPh_4CuCl_3$ has been the subject of a most detailed ESR study [269], which yielded g_{xx} = 2.08, g_{yy} = 2.11, g_{zz} = 2.32, $D = -0.11$ cm^{-1} and $E = 0.009$ cm^{-1}. The average g-value of 2.17 is consistent with the flattened tetrahedral coordination of the metal atoms, and the zero-field splitting has been discussed in some depth [269].

(v) Other systems

$CsCuCl_3$ obeys the Curie—Weiss law down to 55 K, with μ_{eff} = 1.91 B.M. (corresponding to g = 2.21) and $\theta = -3.5$ K [271]. Below 55 K, the susceptibility falls short of Curie—Weiss behaviour, and a sharp peak in the plot of heat capacity against temperature is observed at 10.4 K. These results are interpreted in terms of square coplanar $CuCl_4^{2-}$ ions with linear antiferromagnetic exchange above 10.4 K, and three-dimensional antiferromagnetic exchange at lower temperatures. A subsequent study [272] reported single crystal magnetic anisotropy measurements, which led to g-values of 2.22 parallel to the c axis (about which the Cu atoms form a spiral chain) and 2.18 parallel to the a axis. A model which considered infinite linear chains of S = 1/2 atoms, coupled by an anisotropic Heisenberg interaction, was found to fit the data rather well. Down to about 30 K, nearest-neighbour interactions predominate: at lower temperatures, three-dimensional interactions between chains become important. The nearest-neighbour exchange integral $2J$ is about -6 cm^{-1}. Achiwa [273] used a somewhat different interaction model, and obtained $2J$ values of between -8 and -10 cm^{-1} for nearest-neighbour exchange, depending on the method of calculation. The single crystal susceptibilities [272] show cusps indicative of long-range ordering around 10 K, consistent with the heat capacity measurements.

The first report [142] of the $Cu_2Cl_8^{4-}$ ion in $[Co(en)_3]CuCl_5 \cdot H_2O$ included some measurements: Curie—Weiss behaviour was found in the range 77—300 K, with μ_{eff} = 1.88 B.M. and $\theta = -1$ K. A powder ESR measurement at 77 K showed evidence of spin—spin coupling; the spectrum could be interpreted in terms of a triplet ground state dimer. Low-temperature susceptibility measurements [274] revealed an antiferromagnetic transition at 15.5 K, leading to an exchange integral $2J$ of -17 cm^{-1} for coupling within the dimer. Analysis of the ESR spectrum gave a zero-field splitting D of about 0.02 cm^{-1} for the S = 1 dimer. The most detailed study [275] included single crystal susceptibility data, which produced a revised value for the exchange integral

$2J$ of -14.7 cm^{-1}. Inclusion of a non-zero exchange integral for inter-dimer interactions failed to improve the fit, and it was concluded that such interactions are negligible. The relatively low symmetry of the anion will make a detailed theoretical study of the magnetic exchange interactions rather difficult in this compound; these could well depend on subtleties of bond angles, etc.

Finally in this section, we note that $FeCuCl_4$ (of unknown structure) is antiferromagnetic, with a Neel temperature of 20 K [20].

H. OTHER PHYSICAL METHODS

(i) Nuclear quadrupole resonance

Nuclear quadrupole resonance (NQR) is, in principle, a useful technique in the study of chlorocuprates(II), since ^{35}Cl and ^{37}Cl have nuclear quadrupole moments. The NQR spectrum should distinguish between chemically non-equivalent Cl atoms in a chlorocuprate(II), and the NQR frequencies can be intepreted in terms of the extent to which the Cl atoms are involved in covalent bonding. Moreover, the NQR measurements can detect magnetic ordering at low temperatures.

If we regard the ligands as Cl^- ions which donate pairs of σ-electrons to the metal, the frequencies should increase with the extent of such donation. However, π-donation makes a negative contribution to the frequency. Complications arise with bridging chlorines: the NQR frequency depends on the bridging angle as well as on the bond strengths. However, given NQR data for a wide range of chlorocuprates(II) of known structure, we might hope to see trends in the NQR frequencies which can be interpreted in terms of σ- and π-bonding. Unfortunately, much of the experimental evidence is confusing. One difficulty arises from the temperature dependence of the NQR frequency [276]. In most halide complexes, the frequencies increase on cooling; if, in our series of chlorocuprates(II), the temperature coefficients were roughly the same in all compounds, meaningful comparisons might be made. However, the available data [266,277—279] are very confusing in this respect. The temperature coefficients vary considerably in magnitude and, more importantly, in sign. For a given compound, it is possible for one frequency to increase on cooling and another to decrease; this happens in $[Co(NH_3)_6]CuCl_5$ [278]. Thus a set of NQR frequencies measured at the same temperature are not necessarily comparable. A positive temperature coefficient implies strong d_π—p_π bonding [276]; but attempts to correlate such coefficients with π-bonding lead to some difficulty. For example, in $KCuCl_3$ [266] the temperature coefficients for all three observed frequencies are negative between 1.35 and 77 K, particularly for the lowest-frequency signal which can be assigned, on the basis of Zeeman splitting measurements, to the bridging chlorines in $Cu_2Cl_6^{2-}$: these are believed [188] to be less deeply involved in π-bonding than the terminal chlorines. But in NH_4CuCl_3 [278] the three frequencies all have positive temperature coefficients in the range 77—199 K. Moreover, the lowest-frequency signal (assigned to the bridging chlorines) is found at 11.907 MHz at 77 K, compared with 9.68 MHz at the same temperature in the isostructural $KCuCl_3$; it is difficult to account for these curious results. In several tetragonal tetrachlorocuprates(II) A_2CuCl_4, two signals are observed at about 10—11 MHz and 12 MHz (at 77 K). The lower-frequency band varies little with temperature while the other has a moderately negative temperature coefficient [278]. It is argued [278] that the higher-frequency signal corresponds to the Cl atoms involved in formation of long axial Cu—Cl bonds, and that the larger frequency reflects the degree of σ-covalency in these bonds; this is estimated to be 0.07—0.16 of the covalency in the short terminal bonds, and the variation of this NQR frequency with the known axial bond lengths is rather convincing. However, we need far more NQR data for chlorocuprates(II) before the many doubts and inconsistencies are resolved. A really systematic study is obstructed by the difficulty in observing NQR signals in many chlorocuprates(II). Scaife [278] reports the NQR spectra of six chlorocuprates(II) but lists thirteen more for which signals could not be observed down to 77 K. Studies at liquid helium temperature may help, but the short spin-lattice relaxation times present a serious problem.

Garrett [280] has analysed the NQR spectrum of $CsCuCl_3$; covalency parameters comparable with those obtained from NMR data were deduced (see below).

(ii) Nuclear magnetic resonance

^{133}Cs resonance has been observed in Cs_2CuCl_4 [281]. Nuclear quadrupole coupling tensors and magnetic shift tensors were determined, and in order to account for the quadrupole coupling it was necessary to assume a charge of about +1.1 on the Cu atom. The paramagnetism of the anion led to large isotropic (and smaller anisotropic) shifts.

$CsCuCl_3$ has been studied by ^{35}Cl NMR [282]. It was possible to calculate the nuclear quadrupole coupling tensors for each of the two chemically-equivalent Cl atoms in the crystal, leading to NQR frequencies of 10.929 MHz for the symmetrically bridging chlorines and 11.416 for the others. These values are consistent with the NQR frequencies obtained directly for chlorocuprates(II) [266,277—279]. Covalency parameters for the singly-occupied MO on each metal centre were determined, and found to be in good agreement with those found [204] by MO calculations. ^{63}Cu and ^{65}Cu lines were also found in the NMR spectrum.

(iii) Miscellaneous optical studies

Hirotsu [283] has measured the optical rotatory power and birefringence of $CsCuCl_3$ crystals near the phase transition at 423 K. The optical rotation angle decreases slightly on heating and disappears abruptly at 423 K. The birefringence also undergoes a sharp discontinuity at the phase transition temperature.

We have already mentioned (Sect. E) the application of magnetic circular dichroism to the interpretation of the charge transfer spectrum of $CuCl_4^{2-}$ [210,211]. MCD is helpful in band assignment since the signs of the parameters depend on the symmetries of the ground and excited states. Single-crystal MCD work could help to solve many problems in chlorocuprate(II) spectra.

(iv) Electrical studies

The phase transition at 423 K in $CsCuCl_3$ has been studied by electrical conductivity measurements [183]. A sudden increase in conductivity along the *c*-axis is found just below the transition temperature but no such discontinuity is observed along the *a*-axis. Dielectric constant measurements also exhibit discontinuities in the vicinity of the transition temperature [183].

(v) Thermal studies

Heat capacity measurements have been employed to detect phase transitions, especially magnetic transition at low temperatures, in chlorocuprates(II). Studies have been reported on the ferromagnetic $(RNH_3)_2CuCl_4$ systems [245,250], $CsCuCl_3$ [271] and $(NR_4)_2CuCl_4$ [284]. In $(NMe_4)_2CuCl_4$, a plot of C_p vs. T reveals a sharp peak at 270 K, suggesting a phase transition. In $(Et_4N)_2CuCl_4$, two peaks are observed, at 195 and 260 K. The entropy changes associated with these transitions have been discussed in terms of the orientational disordering of the cation and anion [284].

Differential thermal analysis and differential scanning calorimetry have also been used to study phase transitions in chlorocuprates(II). Work has been reported on $CsCuCl_3$ [144,145], $(Et_2NH_2)_2CuCl_4$ [147], $(NEt_4)_2CuCl_4$ [285] and (*p*-dimethylaminobenzenediazonium)$CuCl_3$ [32].

Thermal conductivity measurements may also reveal phase transitions. In $(MeNH_3)_2CuCl_4$ [247] the plot of conductivity vs. T shows a peak around the transition temperature of ca. 9 K. The variation of the thermal conductivity with temperature is in agreement with the predictions of spin—wave theory for pure magnon conductivity.

The thermal expansion coefficient of $CsCuCl_3$ shows a discontinuity at the transition temperature of 423 K [283].

Blake and Cotton [286,287] have determined the standard enthalpies of complexation ΔH_{com} for $CuCl_4^{2-}$. Using thermochemical data for Cs_2CuCl_4, they found ΔH_{com} to be -2686 kJ mol^{-1}; the procedure involved the calculation of the 'pseudo-lattice energy' of the compound, which requires assumptions concerning the charge distribution. Papatheodorou [288] has reported detailed thermochemical studies on $CsCuCl_3$, Cs_2CuCl_4 and Cs_3CuCl_5. Standard enthalpies of formation were determined by measurements of the enthalpies of solution of the salts in the LiCl/KCl eutectic.

(vi) Miscellaneous

The Mössbauer effect has been used in a study of $FeCuCl_4$ [20]. The results indicate the formulation $Fe(II)Cu(II)Cl_4$ and it is suggested that the compound has a layer structure similar to $FeCl_2$, with six-coordinate iron and antiferromagnetic exchange between Cu and Fe atoms. However, nothing is known about the environment of the copper atoms.

X-ray photoelectron spectra have been obtained for $(NMe_4)_2CuCl_4$ and $(NEt_4)_2CuCl_4$ [289]. Binding energies were measured for metal 2p and for N,C 1s-orbitals. These data are useful in making comparisons with other metal tetrahalide complexes, but it is not clear whether such measurements on chlorocuprates(II) in isolation are likely to be of much value.

I. CHLOROCUPRATES(II) IN SOLUTION

This article is primarily concerned with crystalline chlorocuprates(II), their structures and physical properties. In this section we restrict ourselves to solution work which is directly relevant to solid-state studies and which concerns genuine chlorocuprate(II) species, as opposed to solvated ions. Our coverage here is intended to be illustrative, rather than exhaustive.

(i) Aqueous solutions

The stepwise formation constants K_n for the replacement of water by chloride in the coordination sphere of Cu^{2+} are rather low; the most recent work [290] gives $K_1 = 4.0$, $K_2 = 4.7$, $K_3 = 1.6$ and $K_4 = 0.17$. Thus appreciable concentrations of $CuCl_4^{2-}$ are present in solutions containing a large excess of chloride, but it is not clear whether this species is related to the $CuCl_4^{2-}$ found in crystals, or whether it might be a tetragonal octahedral solvated ion $[CuCl_4(H_2O)_2]^{2-}$. Attempts have been made to analyse the *d—d* spectra of solutions containing Cu^{2+} and Cl^- in the hope of detecting chlorocuprate(II) species whose spectra are known from solid-state work. Spessard [291] performed Gaussian analyses of the rather broad, featureless *d—d* absorption of such solutions; with chloride ion concentrations below 6M, the spectra were consistent with mixtures of tetragonal octahedral $[CuCl_n(H_2O)_{6-n}]^{(2-n)+}$ species, which seems reasonable. At higher chloride concentrations, the absorption could be resolved into two bands at 8.5 and 10.8 kK. Spessard claimed this as evidence for the presence of $CuCl_5^{3-}$ ions. However, the higher energy band in this analysis was several times as intense as the lower energy band, contrary to the relative intensities of the bands in crystals containing

$CuCl_5^{3-}$. In any case, thermodynamic evidence suggests that $CuCl_5^{3-}$ can be present only in minute quantities in aqueous solutions, even with very high chloride concentrations. A more realistic assessment [292] proposes that the hydrated species $[CuCl_n(H_2O)_{6-n}]^{(2-n)+}$ dominate up to chloride concentrations of about 12 M; at higher concentrations of Cl^-, D_{2d} $CuCl_4^{2-}$ ions can be detected and at still higher Cl^- concentrations (ca. 20 M), polymeric species, perhaps hydrated $Cu_nCl_{2n+2}^{2-}$ ions, are present. These conclusions were based on the analysis of electronic spectra, but they have support from X-ray diffraction studies of solutions containing Cu^{2+} and Cl^- [293,294]. It is still uncertain, however, whether unhydrated chlorocuprate(II) anions are ever present in appreciable concentrations in aqueous solution. At any rate, crystalline chlorocuprates are generally decomposed by water, although, as previously noted (Sect. B) they can often be crystallised from aqueous solutions.

(ii) Non-aqueous solvents

In most organic solvents, formation constants for the coordination of Cl^- to Cu^{2+} are much higher than in water, and in non-coordinating solvents we may expect to find genuine chlorocuprate(II) species. In acetonitrile, for example, Manahan and Iwamoto [295] found $\log K_1 = 9.7$, $\log K_2 = 7.9$, $\log K_3 = 7.1$ and $\log K_4 = 3.7$. This is perhaps not the best example of a non-coordinating solvent; Furlani and Morpurgo [296] studied the electronic spectra of various chlorocuprates(II) in CH_3CN and CH_3NO_2, and found some evidence of solvolysis. Even so, they were able to identify the flattened tetrahedral $CuCl_4^{2-}$ ion in solutions containing excess chloride. The solvolysis is apparently endothermic; on heating, the absorption bands shift in a manner consistent with a change to a tetragonally-elongated octahedral solvated species. But the $CuCl_4^{2-}$ ion seems to adopt the same distorted tetrahedral configuration as it does in the solid state.

Ludwig and Textor [168] claimed spectroscopic evidence for $CuCl_3^-$ ions in dichloromethane solutions of trichlorocuprates(II) with large cations such as $AsPh_4^+$. However, the similarity of these spectra to that of the discrete, non-planar $Cu_2Cl_6^{2-}$ dimer (as found in crystalline $AsPh_4CuCl_3$ and PPh_4CuCl_3) must rule out this possibility. It seems fairly clear that chlorocuprates(II) which contain discrete anions in the solid state will dissolve in non-coordinating solvents with retention of the essential configuration of the anion.

The nature of the species present in solutions of $CuCl_2$ in acetic acid containing excess LiCl has been the subject of some discussion. Eswein et al. [297] claim that such solutions contain 'Li_2CuCl_4' in two distinct configurations, one with distorted tetrahedral coordination of the copper atoms and the other with square coplanar coordination; these were characterised by bands at 22 kK and 26 kK respectively. However, Sawada et al. [298] suggest that the square planar form is actually $LiCuCl_3$. In acetic acid, some solvation would not be unexpected but the spectra do suggest the presence of D_{2d} $CuCl_4^{2-}$ ions.

(iii) Fused salts

The *d—d* spectrum of Cu^{2+} in the LiCl—KCl eutectic exhibits a maximum at 9.6 kK, consistent with the presence of flattened CuCl$_4^{2-}$ tetrahedra [299, 300]. In molten CsCl, and in CuCl$_2$—CsCl—2,4-dichlorobenzylphosphonium chloride, the absorption maximum is observed at 8.0 kK, indicating a less-flattened tetrahedron [301]. However, in molten AlCl$_3$ containing Cu^{2+} a band is observed at 11.6 kK [302]; this is taken to indicate tetragonal octahedral coordination, and it is suggested that the absorbing species is Cu(Al$_2$Cl$_7$)$_2$, i.e. Cl$_3$Al—Cl—AlCl$_3$—Cu—Cl$_3$Al—Cl—AlCl$_3$, with the copper at the centre of a distorted octahedron of Cl atoms formed by two pyramidal AlCl$_3$ groups.

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