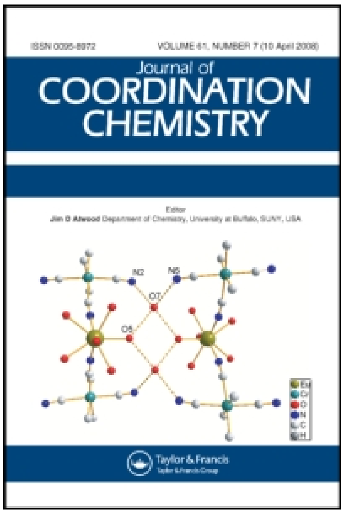

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

TETRAHALO AND (MIXED-TETRAHALO) CUPRATES OF THE 1-METHYL- AND 2-METHYLPIPERAZINIUM DICATIONS. HYDROGEN BONDING EFFECTS ON THE COORDINATION GEOMETRY OF THE CuX_4^{2-} ANIONS

G. Marcotrigiano[a]; L. Menabue[b]; G. C. Pellacani[b]
[a] Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, Bari, Italy [b] Istituto di Chimica Generale ed Inorganica, University of Modena, Modena, Italy

To cite this Article Marcotrigiano, G. , Menabue, L. and Pellacani, G. C.(1979) 'TETRAHALO AND (MIXED-TETRAHALO) CUPRATES OF THE 1-METHYL- AND 2-METHYLPIPERAZINIUM DICATIONS. HYDROGEN BONDING EFFECTS ON THE COORDINATION GEOMETRY OF THE CuX_4^{2-} ANIONS', Journal of Coordination Chemistry, 9: 3, 141 — 149

To link to this Article: DOI: 10.1080/00958977908076520

URL: http://dx.doi.org/10.1080/00958977908076520

J. Coord. Chem., 1979, Vol. 9, pp. 141–149
0095-8972/79/0903-0141$04.50/0

TETRAHALO AND (MIXED-TETRAHALO) CUPRATES OF THE 1-METHYL- AND 2-METHYLPIPERAZINIUM DICATIONS. HYDROGEN BONDING EFFECTS ON THE COORDINATION GEOMETRY OF THE CuX_4^{2-} ANIONS.

G. MARCOTRIGIANO,† L. MENABUE‡ and G. C. PELLACANI‡

†*Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, Via Gentile 182, 70126 Bari, Italy*

‡*Istituto di Chimica Generale ed Inorganica, University of Modena, Via Campi 183, 41100 Modena, Italy*

(Received March 2, 1978; in final form June 14, 1978)

Some halo- and (mixed-halo) cuprates of the type (n-MepipzH$_2$)CuX$_m$Y$_{4-m}$ (X = Cl; Y = Br; m = 4,3,2,1,0; n = 1 and 1-MepipzH$_2$ = 1-methylpiperazinium dication; n = 2 and 2-MepipzH$_2$ = 2-methylpiperazinium dication) and (1-MepipzH·HX)$_2$CuX$_4$ (X = Cl,Br) (1-MepipzH·HX = 1-methylpiperazinium monocation hydrohalide) were prepared and characterized by means of spectroscopic, magnetic, differential scanning calorimetric analysis and conductometric measurements. The compounds in the solid state may be divided in two categories: a) the (1-MepipzH$_2$)CuX$_m$Y$_{4-m}$ (m = 4,3,2,1,0) and (2-MepipzH$_2$)CuX$_m$Y$_{4-m}$ (m = 1,0) complexes, for which a distorted tetrahedral configuration is suggested from their room-temperature spectroscopic properties; b) the (2-MepipzH$_2$)-CuX$_m$Y$_{4-m}$ (m = 4,3,2) and (1-MepipzH·HX)$_2$CuX$_4$ complexes, for which an approximately square-planar geometry may be suggested. In particular the (1-MepipzH·HBr)$_2$CuBr$_4$ compound shows a thermochromic behaviour associable with a change in the coordination geometry like all the complexes in N,N′-dimethylformamide solution. The distortion from tetrahedral symmetry of the complexes is discussed on the basis of extensive N–H · · · X hydrogen bonding interactions, which are proposed as responsible for the planar geometry.

INTRODUCTION

The current interest in the geometry and environment of the tetrahalocuprate(II) anions is derived from the fact that they show a wide variety of structural geometries ranging from square-planar through tetrahedral and onto trigonal bipyramidal.[1]

As with dications interesting geometries of the tetrahalocuprate anions and coordination geometry changes in some CuX_4^{2-} anions were found, we have now investigated the complexes formed between the 1-methyl- and 2-methylpiperazinium dications (hereafter abbreviated as 1-MepipzH$_2$ and 2-MepipzH$_2$ respectively) and the copper halides.

EXPERIMENTAL

Preparation of the Hydrohalide Salts

The 1-methyl- and 2-methylpiperazinium dihydrohalide salts were prepared by dropwise addition of a concentrated hydrogen halide solution to a concentrated ethanolic solution of the amine until complete neutralization of the amine and by evaporating completely the solution obtained. All the salts were recrystallized from methanol and diethyl ether.

Preparation of the Complexes

(1-MepipzH$_2$)CuCl$_4$, (1-MepipzH$_2$)CuCl$_2$Br$_2$ and (2-MepipzH$_2$)CuCl$_2$Br$_2$ were obtained by adding a boiling methanolic solution of the dihydrochloride salt to a warm solution of $CuCl_2 \cdot 2H_2O$ or $CuBr_2 \cdot 3H_2O$ in the $CuCl_4^{2-}$ or $CuCl_2Br_2^{2-}$ anions, respectively, followed by cooling at 4–5°C.

(1-MepipzH$_2$)$_2$CuX$_6$ (X = Cl,Br) complexes were obtained by mixing a boiling methanolic solution of the dihydrohalide salt and of the corresponding metal salt in a 4:1 molar ratio. By cooling at 4–5°C for some hours the solid crystalline compound precipitated.

(n-MepipzH$_2$)CuCl$_3$Br and CuClBr$_3$ were obtained by adding to a boiling ethanolic solution containing a stoichiometric amount of HBr (48%) (1 mM) and the n-MepipzHCl salt (1 mM) an ethanolic solution of $CuCl_2 \cdot 2H_2O$ (1 mM) for the former complex and $CuBr_2 \cdot 3H_2O$ (1 mM) for the latter.

$(2\text{-MepipzH}_2)\text{CuX}_4$ (X = Cl,Br) were prepared by adding a concentrated HCl or HBr solution, respectively, to an ethanolic solution containing 2-methylpiperazine and $\text{CuX}_2 \cdot n\text{H}_2\text{O}$ until the amine was neutralized.

Physical Measurements

The electronic spectra of the solid compounds were recorded with a Beckman DK 1A spectrophotometer in the temperature range 25–110°C. Samples were prepared by grinding the complexes on a filter paper as support. The electronic spectra in N,N′-dimethylformamide (DMF) solution were recorded in a 25–95°C temperature range. The infrared spectra of NaCl or KBr pellets were recorded with a Perkin Elmer 521 (4000–400 cm^{-1}) and the far infrared of nujol mulls with a Perkin Elmer FIS3 (400–60 cm^{-1}) spectrophotometer.

The room-temperature magnetic moments were measured by the Gouy method by using $\text{Ni(en)}_3\text{S}_2\text{O}_3$ as a calibration standard and correcting for diamagnetism with the appropriate Pascal constants.

Differential scanning calorimetric measurements were made with a Perkin Elmer DSC–1 instrument.

The conductivities of the complexes in N,N′-dimethylformamide solution were measured in the temperature range 25–95°C with a WTW (Wissenschaftlich-Technische Werkstatten) D 812 conductivity meter, LBR.

Analyses

Nitrogen, carbon, and hydrogen were analized by Mr. Giuseppe Pistoni using a Perkin Elmer 240 elemental analyzer. Halogens were directly analyzed on the complexes in aqueous solution with the Volhard method.

RESULTS AND DISCUSSION

The analytical results are reported in Table I. All of the compounds are crystalline, stable in air, and soluble in polar organic solvents.

The prepared complexes have empirical formulas of the type $(n\text{-MepipzH}_2)\text{CuX}_m\text{Y}_{4-m}$ (X = Cl and Br; m = 4,3,2,1,0) and of the type $(1\text{-MepipzH}_2)_2\text{CuX}_6$ (X = Cl,Br). In the latter compounds the tetrahalocuprate species may be considered to be present as it is indicated by their spectroscopic results. In particular the charge-transfer bands (which are characteristic of the ligands bonded to the Cu^{2+}) of these complexes are similar to those of the com-

TABLE I
Analytical results.

	Color	Cu %		C %		H %		N %		X %		Mp, °C	μeff B.M.
		calcd	found	calcd	found	calcd	found	calcd	found	calcd	found		
$(1\text{-MepipzH}_2)\text{CuCl}_4$	yellow	20.66	20.86	19.51	19.88	4.59	4.88	9.11	9.34	46.12	45.89	194–7	1.90
$(1\text{-MepipzH}_2)_2\text{CuCl}_6$	yellow-green	13.22	13.35	24.97	25.14	5.87	5.99	11.66	11.61	44.27	43.83	193–6	1.86
$(1\text{-MepipzH}_2)\text{CuCl}_3\text{Br}$	red-orange	18.05	17.29	17.05	18.00	4.01	4.43	7.96	8.06			167–70	1.81
$(1\text{-MepipzH}_2)\text{CuCl}_2\text{Br}_2$	red	16.03	16.17	15.14	15.28	3.56	3.73	7.07	6.85			157–61	1.86
$(1\text{-MepipzH}_2)\text{CuClBr}_3$	red-violet	14.41	14.08	13.61	13.90	3.20	3.36	6.35	6.37			138–42	1.79
$(1\text{-MepipzH}_2)\text{CuBr}_4$	violet	13.09	13.06	12.36	12.41	2.91	2.91	5.77	5.85	65.86	65.42	186–9	1.74
$(1\text{-MepipzH}_2)_2\text{CuBr}_6$	black	8.50	9.10	16.06	16.26	3.78	3.88	7.50	7.44	64.16	64.13	214–7	1.60
$(2\text{-MepipzH}_2)\text{CuCl}_4$	yellow-green	20.66	20.69	19.51	19.08	4.59	4.72	9.11	9.16	46.12	46.43	210 d	1.92
$(2\text{-MepipzH}_2)\text{CuCl}_3\text{Br}$	orange	18.05	18.22	17.05	18.00	4.01	4.32	7.96	8.23			215 d	1.75
$(2\text{-MepipzH}_2)\text{CuCl}_2\text{Br}_2$	red	16.03	16.30	15.14	15.94	3.56	3.73	7.07	7.34			188–91	1.89
$(2\text{-MepipzH}_2)\text{CuClBr}_3$	red-violet	14.41	14.64	13.61	13.76	3.20	3.32	6.35	6.27			176–9	1.80
$(2\text{-MepipzH}_2)\text{CuBr}_4$	violet	13.09	13.22	12.36	11.99	2.91	2.86	5.77	5.57	65.86	66.03	170–3	1.82

plexes containing CuX_4^{2-} species[1] and therefore they may be correctly formulated as $(1\text{-MepipzH}\cdot HX)_2CuX_4$ (X = Cl,Br).

Electronic Spectra and Magnetic Moments

On the basis of the position and of the intensity of the d–d bands in the room-temperature electronic spectra the complexes may be divided into two types, indicated as (a) and (b) which are reported in Tables II and III, respectively, and exemplified in Figure 1.

All the complexes show absorption bands at about 3950, 4260, 4410 and 5180 cm^{-1}, for the 1-MepipzH_2 derivatives, and at about 4000, 4350, 4570, 4780, 5180 and 6900 cm^{-1}, for the 2-MepipzH_2 derivatives (the band at 5180 cm^{-1} disappears on heating). These bands are weak compared to those assigned to the electronic transitions and are probably due to vibrational overtones.

The type (a) complexes show d–d bands (generally two) in the near i.r. at about 6200–7200 and 9200–10100 cm^{-1} which are similar to those reported for compounds which are known to contain CuX_4^{2-} ions in D_{2d} symmetry with a typical tetragonal flattening.[1] The "flattened" tetrahedron with, nearly or exactly, D_{2d} symmetry is a geometry very commonly found for the CuX_4^{2-} anion and is intrinsically more stable than a complex with either T_d (regular tetrahedron) or D_{4h} (square-planar) symmetry.[3,4] This configuration is stabilized by the effect of the ligand–ligand repulsions which offset the crystal-field stabilization.

The room-temperature electronic spectra of the type (b) complexes (Table III) are shifted at higher energies by respect to those of the type (a) (Table II). This suggests that the geometry distorts from a "flattened" tetrahedron (type a)) toward a square-plane one, as it is known that the electronic absorption spectrum is sensitive to the amount of "flattening" or distortion that has occurred(5). Furthermore the type (b) complexes show spectra very similar to those of other tetrahalocuprate anions having an approximately square-planar configuration (5–7). The shape and position of the d–d bands further suggest that the (2-MepipzH_2)-

TABLE II
Electronic spectra (cm^{-1}) of the solid tetrahalo- and (mixed-tetrahalo) cuprates having distorted tetrahedral symmetries

	d–d bands		Charge-transfer bands		
$(1\text{-MepipzH}_2)CuCl_4$	7140	10100	25640		
$(1\text{-MepipzH}_2)CuCl_3Br$	7140	9800	22220sh		
$(1\text{-MepipzH}_2)CuCl_2Br$	7040	9800	17540sh	21740	
$(1\text{-MepipzH}_2)CuClBr_3$	6700	9800	16950sh	20410	
$(1\text{-MepipzH}_2)CuBr_4$	6600 7300	9800	17240sh	19610	23810sh
$(2\text{-MepipzH}_2)CuClBr_3$	6250	9260	17540	20000	
$(2\text{-MepipzH}_2)CuBr_4$	6670	10000	16950sh	19610	24100sh

TABLE III
Electronic spectra (cm^{-1}) of the solid halocuprates having an approximately square-planar symmetry

	d–d bands		Charge-transfer bands			
$(1\text{-MepipzH}\cdot HCl)_2CuCl_4$	10420		26320			
$(1\text{-MepipzH}\cdot HBr)_2CuBr_4$[a]	7690	10100	16950	19050sh	22220	26760sh
$(2\text{-MepipzH}_2)CuCl_4$	10200sh	12350	22730sh	27400sh		
$(2\text{-MepipzH}_2)CuCl_3Br$	10000sh	12120	20000sh	27400		
$(2\text{-MepipzH}_2)CuCl_2Br_2$	10000sh	12050	18520sh	25000		

[a] This complex may be considered having a coordination/geometry intermediate between type a) and b) complexes.

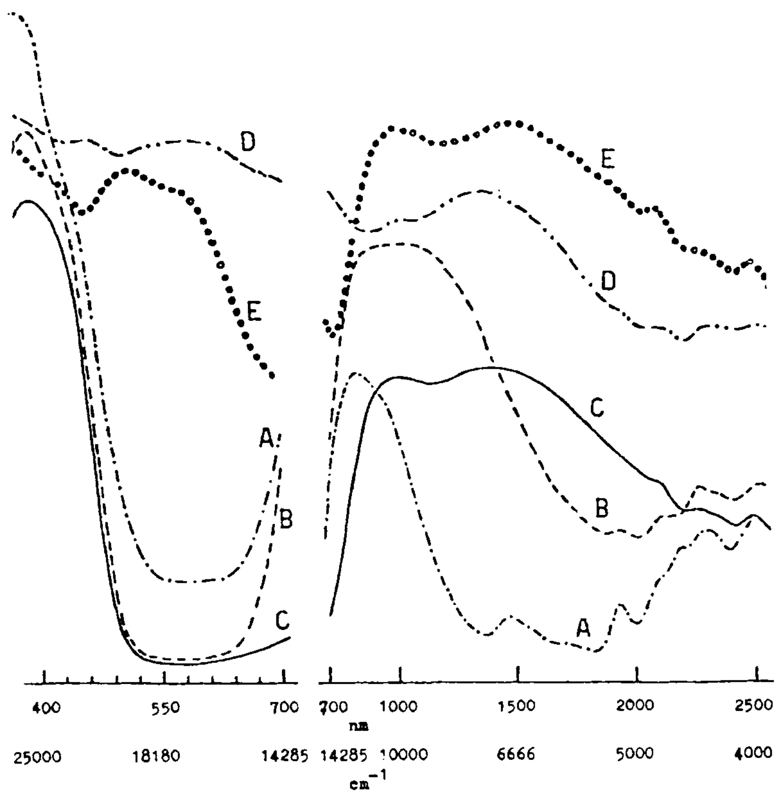

FIGURE 1 Solid electronic spectra of the type a) (distorted tetrahedral) (1-MepipzH$_2$)CuCl$_4$ (C) and (1-MepipzH$_2$)CuBr$_4$ (E) complexes, of the type b) (approximately square-planar) (2-MepipzH$_2$)CuCl$_4$ (A) and (1-MepipzH·HCl)$_2$CuCl$_4$ (B) and of the (1-MepipzH·HBr)$_2$CuBr$_4$ (D) complexes.

CuX_mY_{4-m} (X = Cl; Y = Br; m = 4,3,2) complexes are more distorted than the (1-MepipzH·HX)$_2$ CuX$_4$ (X = Cl,Br) complexes. The configuration of the latter complexes may be considered intermediate between type (a) and (b) complexes.

From these data we may draw some conclusions: 1°) for the complexes of anion/cation 1/1 stoichiometric ratio, only the 2-methylpiperazinium dication gives complexes of approximately square-planar configuration; 2°) the distortion of the 2-methylpiperazinium dication complexes diminishes when the chloride atom number of the anion diminishes; 3°) with the 1-methylpiperazinium dication the complexes have symmetry distorted from the "flattened" tetrahedron only with an anion/cation stoichiometric ratio of 1/2.

Therefore the distortion of the complexes may mostly be ascribed to the different hydrogen bonding ability of the cations. In fact the cations, which have similar dimension, may only differ in hydrogen bonding ability, which is greater in the 2-methylpiperazinium than in the 1-methylpiperazinium cation, being in the latter cation the methyl group directly linked on a nitrogen atom. The extensive N–H · · · X hydrogen bonding reduces the effective charge on the halide atoms and causes the prevailing effect of the crystal field stabilization on the ligand–ligand repulsion.[8,9]

The differential scanning calorimetric and thermogravimetric analysis measurements between 20°C and the melting point temperature of the type (b) complexes give an idea of the role and strength of the hydrogen bonding in stabilizing an approximately square-planar configuration. In fact only the (1-MepipzH·HBr)$_2$CuBr$_4$ complex, in which are present N–H · · · Br hydrogen bonds weaker than the N–H · · · Cl hydrogen bonds present in the other type b) complexes, shows a reversible, first-order phase transition (thermochromism) (Figure 2, Table IV), which may involve a definite change in structure. This geometry change is favoured by a weakening of the hydrogen bonding network as a result of the increasing disorder due to thermal motion. The high-temperature form of this complex may be tentatively

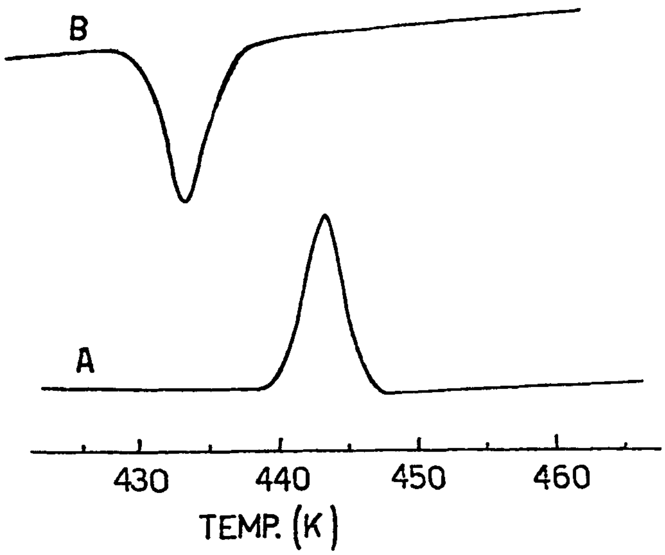

FIGURE 2 Differential scanning calorimetric results during (A) heating and (B) cooling scans of the $(1\text{-MepipzH·HBr})_2CuBr_4$ complex.

TABLE IV

Transition data of the $(1\text{-MepipzH·HBr})_2CuBr_4$

T_{initial}	440°K
T_{final}	446°K
$T_{\text{transition}}$	443°K
Enthalpy of transition	9.62 kJmole^{-1}

(as unfortunately we are unable to record its electronic spectrum above the temperature of the phase transition), but reasonably suggested to have a symmetry similar to that of the type (a) complexes.

The qualitative value of the extent of distortion of the $CuCl_4^{2-}$ anions may be approximately obtained by calculating the average of the two large (greater than 109° 47′) Cl–Cu–Cl angles from the maximum d–d transition, as proposed by R. L. Harlow and coll.,[5] considering the compounds to be truly four-coordinate. The values obtained are about 150° for the $(2\text{-MepipzH}_2)CuCl_4$ and about 140° for the $(1\text{-MepipzH·HCl})_2CuCl_4$ complexes.

The N,N′-dimethylformamide (DMF) solution behaviour of all the complexes is rather unusual. The temperature appears to be the major factor determining the changes in the geometry around the metal ion, while the cations present have an identical effect. For all the complexes (Table V) we observe a broad band at about 9500 cm^{-1}, which may be assigned to a d–d transition, and some bands above 15000 cm^{-1}, which may be assigned to charge-

TABLE V

Conductivity measurements (S cm^2 mol^{-1}) of the complexes in DMF solution in the 298–368°K temperature range[a]

	298°K	318°K	338°K	358°K	368°K	358°K	338°K	318°K	298°K
$(1\text{-MepipzH}_2)CuCl_4$	37	46	57	66	81	72	61	53	43
$(1\text{-MepipzH}_2)CuCl_3Br$	45	56	66	83	102	96	84	71	60
$(1\text{-MepipzH}_2)CuCl_2Br_2$	51	60	73	94	117	111	96	79	71
$(1\text{-MepipzH}_2)CuClBr_3$	54	66	82	102	125	117	103	87	73
$(1\text{-MepipzH}_2)CuBr_4$	61	77	96	120	138	123	105	90	75
$(1\text{-MepipzH·HCl})_2CuCl_4$	44								
$(1\text{-MepipzH·HBr})_2CuBr_4$	91								
$(2\text{-MepipzH}_2)CuCl_4$	39	47	59	75	86	78	64	53	44
$(2\text{-MepipzH}_2)CuCl_3Br$	43	52	60	75	96	90	78	63	55
$(2\text{-MepipzH}_2)CuCl_2Br_2$	53	61	71	90	108	102	90	75	63
$(2\text{-MepipzH}_2)CuClBr_3$	57	63	78	99	117	108	93	79	66
$(2\text{-MepipzH}_2)CuBr_4$	57	72	93	111	126	118	103	97	72

[a] Upon heating the complexes partially decompose (solvolyse?) (10–20%), as the cooling values are greater than the heating values obtained at the same temperature, and as the spectra of the CuX_4^{2-} ions disappear.

transfer transitions, as they are strictly dependent on the atoms bonded to the metals. In particular these charge-transfer bands are characteristic of the tetrahalo-species.[1] When the temperature increases the d–d band splits into two bands, while the charge-transfer bands shift toward lower energies (Figure 3 exemplifies this situation). The experimental data suggest an explanation of this thermochromic behaviour of the solution complexes, as in the case of the solid (1-MepipzH·HBr)$_2$CuBr$_4$ complex, as the result of a nearly reversible change in the coordination geometry,[10–12] favoured by the increasing disorder due to the thermal motion. The high temperature form of the solution complexes presents a lower distorted tetrahedral symmetry than the room-temperature form.

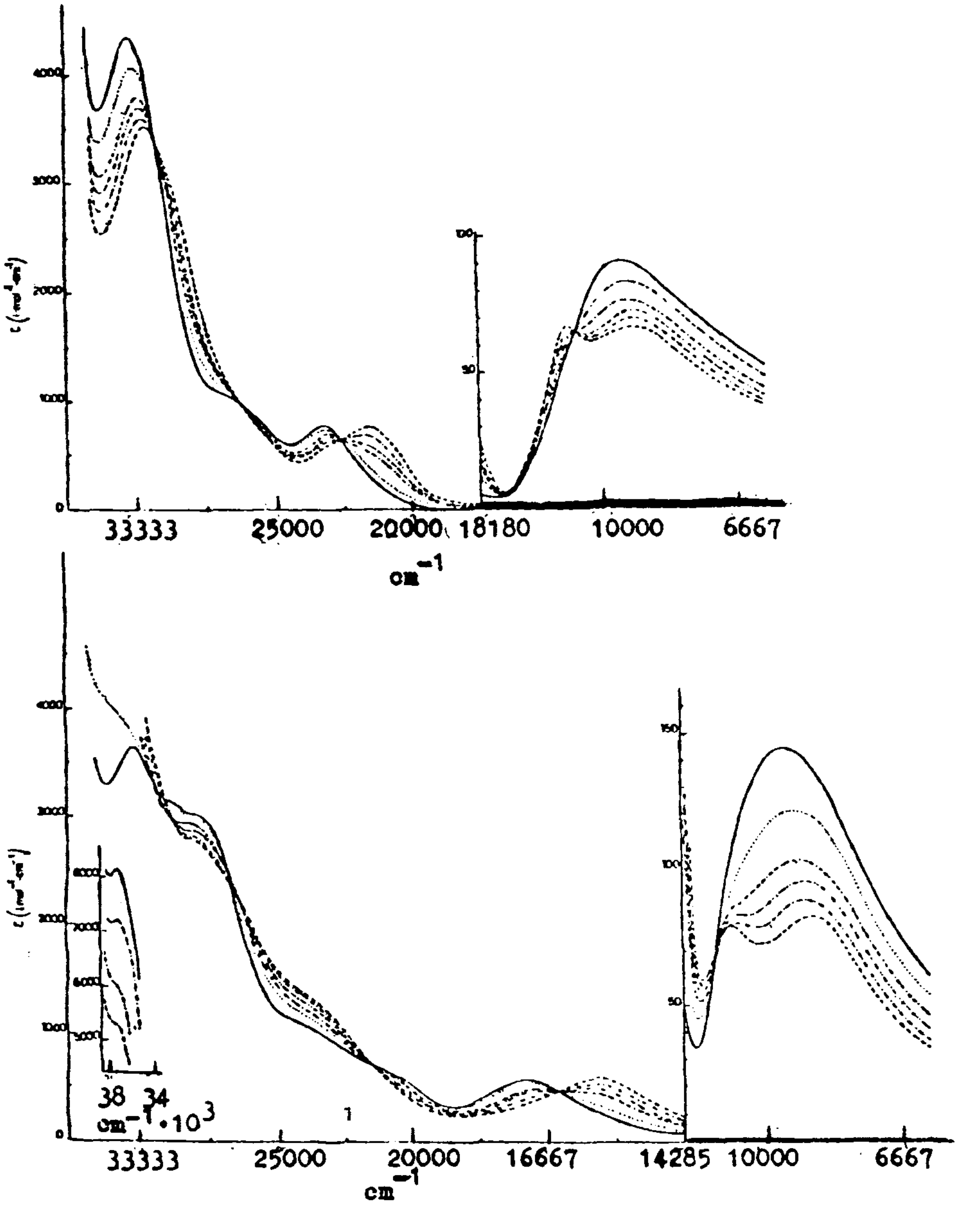

FIGURE 3 Exemplifying DMF solution electronic spectra of the (2-MepipzH$_2$)CuCl$_4$ (above) and (2-MepipzH$_2$)CuBr$_4$ (below) complexes at 368°K(— — — —), 358°K(— · — · —), 348°K(·· — ·· —), 338°K(— · — — ·), 318°K(······) and 298°K(——).

TABLE VI

Far-i.r. spectra (400–60 cm^{-1}) of the dihydrohalide salts, their tetrahalo- and (mixed-tetrahalo) cuprates

	Approx. geom.	υ(CuCl)	υ(CuBr)	δ(CuX)	Other far-i.r. bands
1-Mepipz$(HBr)_2$					365m 269m 238m 152ms 112ms 64s
(1-MepipzH_2)$CuCl_4$	D_{2d}	300s 274ms 230sh		187s	329ms 212ms 140w 118s 81m
(1-MepipzH_2)$CuCl_3Br$	C_s^a	280sh 270s	228wb	170mb 138sh	338m 302ms 106m 88m
(1-MepipzH_2)$CuCl_2Br_2$	C_{2v}^a	285s 266sh	235ms(208mb)	160m 138w	336m 306sh(208mb) 80m
(1-MepipzH_2)$CuClBr_3$	C_s^a	284ms	234s 216m	158m 140w	335m 263m 204sh 114vw 80m
(1-MepipzH_2)$CuBr_4$	D_{2d}		238s(212s)	140m 120sh	335m 265sh 220sh(212s) 157m 120sh 80ms
(1-MepipzH·HCl$)_2CuCl_4$	D_{2h}	294vs		184s	330m 210ms 140w 116s 79ms
(1-MepipzH·HBr$)_2CuBr_4$	D_{2h}		216mb	136ms	364w 316w 265w 160m 94w
2-Mepipz$(HBr)_2$					370w 318w 308sh 300ms 278vs 194vs 135m 117vs 91vs 64vs
(2-MepipzH_2)$CuCl_4$	D_{2h}	290sh 254vsb		174sb	334m 304ms 204w 138w 100vw 64ms
(2-MepipzH_2)$CuCl_3Br$	C_{2v}^b	284sh 254vs	195w	170mb 140w	335m 304sh 60m
(2-MepipzH_2)$CuCl_2Br_2$	C_{2v}^c	280s 250vs	200w 184w	140wb	331m 240sh
(2-MepipzH_2)$CuClBr_3$	C_s^a	257ve	234sh 184w	160w	340w 330w 98mb
(2-MepipzH_2)$CuBr_4$	D_{2d}		236sh 220s	136sh 124m	334w 317w 262m 183sh 88m

[a] The tetrahedral C_s symmetry for the CuX_3Y^{2-} predicts three i.r.-active Cu–X and one i.r.-active Cu–Y stretching modes; tetrahedral C_{2v} symmetry predicts two i.r.-active Cu–Cl and two i.r.-active Cu–Br stretching modes.

[b] Planar C_{2v} symmetry predicts three i.r.-active Cu–Cl and one i.r.-active Cu–Br stretching modes.

[c] Cis-planar C_{2v} symmetry predicts two i.r.-active Cu–Cl and two i.r.-active Cu–Br stretching modes.

The presence of rather well-defined isosbestic points may confirm the presence in solution of an equilibrium involving only two species, each having a characteristic absorption, which differ only for the coordination geometry.

The molar conductivities (Table V) agree with the above results. The existence of an outer-sphere association between the cation and the anion due to hydrogen bonding interactions decreases when the temperature and bromine atom numbers increase.

The room-temperature magnetic moments of the solid complexes (Table I) agree well with the proposed configurations.[1,2] The low magnetism of the $(1\text{-MepipzH}\cdot\text{HBr})_2\text{CuBr}_4$ may be ascribed to a weak coupling, suggesting the presence of interactions among the CuBr_4^{2-} anions.

Far-infrared Spectra

The far-i.r. spectra of the complexes and of the appropriate starting amine hydrohalide salts are listed in Table VI.

The spectrum of the $(1\text{-MepipzH}_2)\text{CuCl}_4$ strictly agrees with those of the CuCl_4^{2-} ions for which a D_{2d} symmetry was unequivocally recognized[1,9] and it may be assigned analogously.

The band which appears at 230 cm^{-1} in the $(1\text{-MepipzH}_2)\text{CuCl}_4$ complex, which is a frequency typical of D_{2d} ions,[9] is shifted at 174–184 cm^{-1} in the spectra of the $(1\text{-MepipzH}\cdot\text{HCl})_2\text{CuCl}_4$ and $(2\text{-MepipzH}_2)\text{CuCl}_4$ complexes, in agreement with the distortion of the latter complexes from the D_{2d} symmetry. In fact the b_2 stretching mode of the D_{2d} ion becomes a b_{1u} bending mode and should therefore decrease in energy as the tetrahedron is flattened. toward square-plane.[1,9]

Strong differences between the $(1\text{-MepipzH}_2)\text{CuX}_4$ and $(1\text{-MepipzH}\cdot\text{HX})_2\text{CuX}_4$ (X = Cl,Br) are also found in the stretching bands, which are two for the former and only one for the latter compounds, as is exemplified in Figure 4.

The splitting of the e vibration mode of the $(n\text{-MepipzH}_2)\text{CuBr}_4$ (n = 1,2) also indicates that some distortions from D_{2d} symmetry must be present, wherefore the symmetry is probably further reduced to C_s.

The far-i.r. spectra of the $(2\text{-MepipzH}_2)\text{CuX}_m\text{Y}_{4-m}$ (X = Cl; Y = Br; m = 4,3,2,1) are confused between 300 and 200 cm^{-1} as in this spectral region strong ligand absorptions also appear. However the stretching Cu–Cl bands are assigned to the more intense vibrations and although they appear at lower frequencies than those normally found for tetrachlorocuprates,[1,2,9] they are yet in the range foreseeable for these vibrations.[1] Furthermore our cations are large enough to form distorted tetrahedral CuX_4^{2-} ions (type a) complexes) preventing the CuX_4^{2-} ions from interacting to produce distorted square-pyramidal or octahedral coordination.[5] Therefore interactions may also be excluded in the type (b) complexes, the distortion of which may be only due to the increasing hydrogen bonding possibility. This and the fact that the Cu–Cl stretching in the distorted tetrahedral $(2\text{-MepipzH}_2)\text{CuClBr}_3$ also appears at 257 cm^{-1}, confirm our assignment, excluding the possibility that these bands may originate from bridging Cu–Cl.

The far-i.r. spectra of the mixed tetrahalocuprates are assigned on the basis of the symmetries suggested from their electronic spectra, as reported in the footnotes of Table VII.

Hydrogen Bonding

The attempt to find evidence for the presence of hydrogen bonding in the complexes by comparing their i.r. spectra with those of the hydrohalide salts, is not conclusive as the salts are also involved in strong hydrogen bonding. However two facts may be considered:

1) in the amine dihydrohalide the N–H motions are assigned to the complex series of bands which appear at 2900–3000 ($\nu(\overset{+}{\text{N}}\text{H}_2)$) and 2670–2400 ($\nu(\overset{+}{\text{N}}\text{H})$) cm^{-1} in the 1-MepipzH_2 dication and at 2850–2950 cm^{-1} ($\nu(\overset{+}{\text{N}}\text{H}_2)$) in the 2-MepipzH_2 dication, as these bands are attenuated on deuteration,[13,14] while the bending modes may be assigned to the bands appearing at 1550–80 and 1540–50 cm^{-1}, respectively. By complex formation the stretching bands are shifted at higher and the bending at lower energies greater in the 1-MepipzH_2 complexes (3055–80, 1515–42 cm^{-1}) than in the 2-MepipzH_2 complexes (3030–60, 1530–46 cm^{-1}), which may confirm that weaker hydrogen bonds are formed with the former than with the latter cation;

2) the N–H bending modes of the $(1\text{-MepipzH}_2)\text{CuX}_4$ complexes are found at 1538 (X = Cl) and 1535 (X = Br) cm^{-1}, while those of the $(1\text{-MepipzH}\cdot\text{HX})_2\text{CuX}_4$ complexes are observed at 1515 (X = Cl) and 1525 (X = Br) cm^{-1} suggesting that more extensive hydrogen bonds are involved in the latter than in the former complexes.

ACKNOWLEDGMENTS

The authors are grateful to the Centro Strumenti of the University of Modena for the recording of the infrared spectra.

REFERENCES

1. D. W. Smith, *Coord. Chem. Rev.*, 21, 93 (1976) and Ref. cited therein.
2. (a) G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem.*, 15, 2333 (1976). (b) G. Marcotrigiano, L. Menabue and G. C. Pellacani, *J. Coord. Chem.*, 5, 189 (1976).
3. D. W. Smith, *J. Chem. Soc. (A)*, 2900 (1970).
4. J. Demuynck, A. Veillard and U. Wahlegren, *J. Amer. Chem. Soc.*, 95, 5563 (1973).
5. R. L. Harlow, W. J. Wells, III, G. W. Watt and S. H. Simonsen, *Inorg. Chem.*, 14, 1768 (1975) and Ref. cited therein.
6. R. D. Willett, *J. Chem. Phys.*, 44, 39 (1966).
7. R. D. Willett and O. L. Liles, Jr., *Inorg. Chem.*, 6, 1666 (1967).
8. G. Felsenfeld, *Proc. R. Soc. London, Ser. A*, 236, 506 (1956).
9. R. D. Willett, J. R. Ferraro and M. Choca, *Inorg. Chem.*, 13, 2919 (1974).
10. A. R. Chughtai and R. N. Keller, *J. Inorg. Nucl. Chem.*, 31, 633 (1969).
11. K. Sawada, H. Ohtaki and M. Tanaka, *J. Inorg. Nucl. Chem.*, 34, 3455 (1972).
12. G. P. Smith and T. R. Griffiths, *J. Amer. Chem. Soc.*, 85, 4051 (1963).
13. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, N.Y., 1959, p. 259.
14. N. B. Colthrum, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, N.Y., 1964, p. 282.