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Spectroscopic Investigation on Tetrahalo- and Mixed-tetrahalocuprates of the N-Methylpiperidinium and N,N'-Dimethylpiperazinium Cations

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Some tetrahalo- and mixed-tetrahalocuprates of the type $(LH)_2CuCl_mBr_{4-m}$ *and* $(LH_2)CuCl_mBr_{4-m}$ *(m = 4, 3, 2, 1, 0; LH = N-methylpiperidinium cation;* LH_2 *= N,N'-dimethylpiperazinium dication) were prepared and investigated by means of spectroscopic (u.v., vis., near i.r., far-i.r.), magnetic and e.p.r. measurements. The results indicate for all the complexes a distorted tetrahedral configuration, the complexes of the N,N'-dimethylpiperazinium dication being more distorted than those of the N-methylpiperidinium cation. A series based on the hydrogen bonding ability of the counter cation, which takes into account counter cations as morpholinium, piperidinium and piperazinium and some of their derivatives, is also proposed.*

Introduction

Our previous studies on the tetrahalo- and mixed-tetrahalocuprates of the piperidinium, morpholinium and piperazinium cations [1] and of the N-ethylmorpholinium cation [2] emphasized a relation between the hydrogen bonding ability of the cation and the coordination geometry of the metal ion.

In this paper we have considered the effects of the N-methylpiperidinium cation and of the N,N'-dimethylpiperazinium dication (hereafter abbreviated as 1-MepipdH and 1,4-MepipzH_2, respectively) on the metal ion configuration. Of the compounds reported here only the analyses and magnetic moments of the (1,4-MepipzH_2)$CuBr_4$ complex are known [3].

Experimental

Preparation of the Hydrohalide Salts

The hydrohalide salts were prepared by adding an excess of concentrated hydrogen halide solution to an amine solution in water. By complete evaporation the solution separated the hydrohalide salts, which were recrystallized from ethanol or methanol.

Preparation of the Complexes

The $(1\text{-MepipdH})_2CuCl_mBr_{4-m}$ (m = 4, 3, 2) complexes were prepared by mixing an ethanolic $CuCl_2 \cdot 2H_2O$ (1 m*M*) solution to an ethanolic 1-MepipdHCl (2 m*M*) (m = 4) or 1-MepipdHCl (1 m*M*) + 1-MepipdHBr (1 m*M*) (m = 3) or 1-MepipdHBr (2 m*M*) (m = 2) solution. By cooling all the compounds separated, except for the $(1\text{-MepipdH})_2CuCl_2Br_2$ complex, which separated an oil from which the compound precipitated on adding isopropanol.

The $(1\text{-MepipdH})_2CuClBr_3$ complex were separated as previously described by mixing $CuBr_2 \cdot 3H_2O$ (1 m*M*) and 1-MepipdHCl (1 m*M*) + 1 MepipdHBr (1 m*M*), while the $(1\text{-MepipdH})_2CuBr_4$ complex by mixing $CuBr_2 \cdot 3H_2O$ (1 m*M*) and 1-MepipdHBr (2 m*M*) in ethanol + isopropanol (1 + 1).

(1,4-MepipzH_2)$CuCl_4$ complex was separated by mixing $CuCl_2 \cdot 2H_2O$ and an excess of N,N'-dimethylpiperazine in ethanol and by adding a strong excess of concentrated hydrogen chloride.

The (1,4-MepipzH_2)$CuCl_mBr_{4-m}$ (m = 3, 2, 1, 0) complexes instantaneously precipitated by adding a methanolic $CuCl_2 \cdot 2H_2O$ (1 m*M*) solution to a methanolic 1,4-MepipzHCl (1 m*M*) + HBr (48%) (1 m*M*) (m = 3) or 1,4-MepipzHBr (1 m*M*) (m = 2) solution or by adding a methanolic $CuBr_2 \cdot 3H_2O$ (1 m*M*) solution to a methanolic 1,4-MepipzHBr (1 m*M*) + HCl (37%) (1 m*M*) (m = 1) or 1,4-Mepipz$(HBr)_2$ (1 m*M*) (m = 0) solution.

Physical Measurements

The electronic spectra of the solid compounds were recorded on a Shimadzu MPS 50L spectrophotometer. Samples were prepared by grinding the complexes on a filter paper or lens cleaning paper as support. The infrared spectra of KCl or KBr pellets (4000–400 cm^{-1}) or nujol mulls (600–60 cm^{-1}) were recorded on a Perkin-Elmer 180 spectrophotometer. The room temperature magnetic moments were measured by the Gouy method, using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The e.p.r. spectra were

TABLE I. Analytical Results.

	Color	C %		H %		N %		X %		M.P. °C
		calcd	found	calcd	found	calcd	found	calcd	found	
$(1\text{-MepipdH})_2CuCl_4$	yellow	35.50	35.52	6.96	7.30	6.91	6.92	34.97	34.84	112–5
$(1\text{-MepipdH})_2CuCl_3Br$	orange	31.99	31.47	6.27	6.30	6.22	6.01			115–8
$(1\text{-MepipdH})_2CuCl_2Br_2$	red	29.12	28.97	5.71	5.75	5.66	5.66			118–21
$(1\text{-MepipdH})_2CuClBr_3$	red-violet	26.72	26.27	5.24	5.23	5.20	5.94			103–6
$(1\text{-MepipdH})_2CuBr_4$	violet	24.68	24.76	4.84	4.86	4.80	4.83	54.79	55.02	125–8
$(1,4\text{-MepipzH}_2)CuCl_4$	yellow	22.39	22.18	5.02	5.15	8.71	8.77	44.11	43.60	182–5
$(1,4\text{-MepipzH}_2)CuCl_3Br$	orange	19.67	19.46	4.41	4.63	7.65	8.12			187–91
$(1,4\text{-MepipzH}_2)CuCl_2Br_2$	red-brown	17.54	17.94	3.93	4.13	6.83	6.83			190–4
$(1,4\text{-MepipzH}_2)CuClBr_3$	red-violet	15.83	15.63	3.54	3.56	6.16	5.97			205–8
$(1,4\text{-MepipzH}_2)CuBr_4$	violet	14.42	14.44	3.23	3.37	5.61	5.67	64.02	64.47	217–21

TABLE II. Room Temperature Electronic Spectra (cm^{-1}) of the Solid Compounds.

	d–d Bands		C.T. Bands				
$(1\text{-MepipdH})_2CuCl_4$	6170	9090	21980sh	24390	30770sh	33900	42550
$(1\text{-MepipdH})_2CuCl_3Br$	6250	8930	20830sh	22730	30120sh	33330	42190
$(1\text{-MepipdH})_2CuCl_2Br_2$	6210	8930	16670sh	20490	31250	41320	
$(1\text{-MepipdH})_2CuClBr_3$	6170	8930	16130sh	19050	27030	38170	
$(1\text{-MepipdH})_2CuBr_4$	5950	9090	16000sh	18180	23530	36770	44050
$(1,4\text{-MepipzH}_2)CuCl_4$	6330	9430	21740sh	24390	28570sh	33670	41670
$(1,4\text{-MepipzH}_2)CuCl_3Br$	5810	9260	19230sh	22220	24270sh	32050	40490
$(1,4\text{-MepipzH}_2)CuCl_2Br_2$	6210	9350	17240sh	20490	31770	39220	
$(1,4\text{-MepipzH}_2)CuClBr_3$	5880	9090	16340sh	19050	23530sh	28570	37740
$(1,4\text{-MepipzH}_2)CuBr_4$	6170	9090	16130sh	18590	23530sh	27780	37040

recorded on a Jeol PE-3X spectrometer. Quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated with diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as a field marker.

Analyses

Nitrogen, carbon and hydrogen were analyzed by Mr. Giuseppe Pistoni using a Perkin-Elmer 240 Elemental Analyser. Halogens were directly analyzed on the complexes in aqueous solution with Volhard's method.

Results and Discussion

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

The room temperature electronic spectra of the solid complexes are reported in Table II. They show two d–d bands in the near-infrared region at 5800–6400 and 8900–9500 cm^{-1}. As the spectra are nearly identical to one another we may conclude that all the complexes must have also similar structures. The shape and positions of the d–d bands of our complexes are also strictly similar to those reported for other compounds, which are known to contain $(CuCl_4)^{2-}$ ions with a typical "flattened" tetrahedral geometry (D_{2d} symmetry) [4], for which we may suggest a distorted tetrahedral configuration for all the complexes reported in this paper. The flattened tetrahedron with a nearly or exactly D_{2d} symmetry is intrinsically more stable than a complex with either T_d (regular tetrahedron) or D_{4h} (square-planar) symmetry [5, 6].

In our complexes ligand–ligand repulsions prevail on the crystal field stabilization due to the scant ability of the counter ions to exert such an extensive hydrogen bonding as to influence the geometry of the $(CuX_4)^{2-}$ ions [7–10]. Since the maximum d–d transition of the complexes should increase in energy as the geometry distorts from a regular tetrahedron toward a square-plane [11], we may recognize that the hydrogen bonding ability of the $1,4\text{-MepipzH}_2$ dication is slightly greater than that of the 1-MepipdH cation.

By comparing the second d–d band of the electronic spectra of the complexes containing the $(CuCl_4)^{2-}$ anions we may propose a series of cations based on their hydrogen bonding ability:

morpholinium cation(12500) [1a] > 2-methylpiperazinium dication(12350) [12] > piperazinium monohydrochloride cation(11490) [1b] > 2-methylpiperazinium monohydrochloride cation(10420) [12] > 1-methylpiperazinium dication(10100) [12] > piperidinium cation(9710) [1a] > piperazinium dication(9620 [1b] > N-ethylmorpholinium cation·(9520) [1c] > 1,4-dimethylpiperazinium dication-(9430) > 1-methylpiperidinium cation(9090)

This series appears to be not unreasonable

The charge-transfer bands of the complexes are also reported in Table II and exemplified in Fig 1

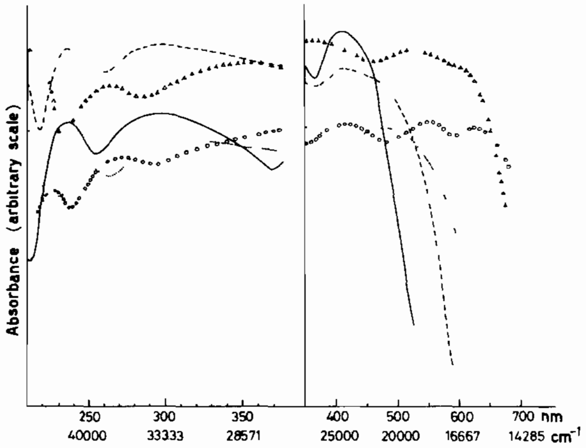

Fig 1 Solid electronic spectra in the charge-transfer region of $(1,4\text{-MepipzH}_2)\text{CuCl}_4$ (——), $(1,4\text{-MepipzH}_2)\text{CuCl}_3\text{Br}$ (– – –), $(1,4\text{-MepipzH}_2)\text{CuCl}_2\text{Br}_2$ (•••), $(1,4\text{-MepipzH}_2)\text{CuClBr}_3$ (ΔΔΔ) and $(1,4\text{-MepipzH}_2)\text{CuBr}_4$ (○○○)

The charge-transfer spectra of the complexes again agree with previous reports, which however regard only the $(\text{CuX}_4)^{2-}$ (X = Cl, Br) anions [13–15] In particular the charge-transfer bands (which are characteristic of the ligands bonded to the Cu^{2+}) of these complexes clearly indicate that the mixed-complexes are true compounds and not mixtures of $(\text{CuCl}_4)^{2-}$ and $(\text{CuBr}_4)^{2-}$ anions

TABLE III Magnetic Moments and Electron Paramagnetic Resonance Data of the Copper(II) Complexes[a]

	μ_{eff} B M	$g_\parallel$	$g_\perp$	$\langle g\rangle$[b]
$(1\text{-MepipdH})_2\text{CuCl}_4$	1 88			2 197
$(1\text{-MepipdH})_2\text{CuCl}_3\text{Br}$	1 81			2 113
$(1\text{-MepipdH})_2\text{CuCl}_2\text{Br}_2$	1 83			2 093
$(1\text{-MepipdH})_2\text{CuClBr}_3$	1 79			2 086
$(1\text{-MepipdH})_2\text{CuBr}_4$	1 85			2 073
$(1,4\text{-MepipzH}_2)\text{CuCl}_4$	1 90	2 313	2 053	2 140
$(1,4\text{-MepipzH}_2)\text{CuCl}_3\text{Br}$	1 85	2 329	2 039	2 136
$(1,4\text{-MepipzH}_2)\text{CuCl}_2\text{Br}_2$	1 77	2 300	2 028	2 119
$(1,4\text{-MepipzH}_2)\text{CuClBr}_3$	1 75			2 119
$(1,4\text{-MepipzH}_2)\text{CuBr}_4$	1 71			2 106

[a] Recorded on polycrystalline samples at room temperature
[b] $\langle g\rangle = 1/3(g_\parallel + 2g_\perp)$

Magnetic moments and e p r spectral parameters are summarized in Table III The room temperature magnetic moments of the solid complexes agree well with the proposed configuration [4, 16, 17]

Polycrystalline samples of copper(II) complexes show two types of resonance in their e p r spectra, the lines at higher field being more intense Therefore the symmetry appears to be always isotropic for all the complexes, except for $(1,4\text{-MepipzH}_2)\text{CuCl}_m\text{Br}_{4-m}$ (m = 4, 3, 2) complexes, which show axial symmetry The room temperature e p r spectrum of a polycrystalline sample of $(1,4\text{-MepipzH}_2)\text{CuCl}_4$ complex is reported as example in Fig 2

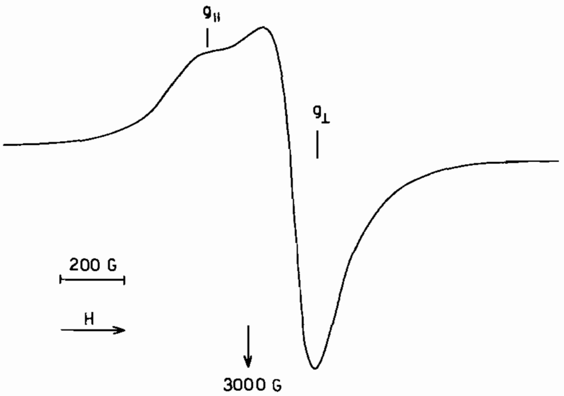

Fig 2 Room temperature e p r spectra of a polycrystalline sample of the $(1,4\text{-MepipzH}_2)\text{CuCl}_4$ complex

In all the spectra the hyperfine splitting is not resolved The *g* values are compared with those of the planar $(\text{N-mph})_2\text{CuCl}_4$ complex (dihedral angle = 0°) (g_z = 2 221, $g_x = g_y$ = 2 040) [18] and of the distorted tetrahedral Cs_2CuCl_4 (dihedral angle = 67 9° [19]) ($g_\parallel$ = 2 384, $g_\perp$ = 2 094) [20] The *g* values of our complexes are close to that of Cs_2CuCl_4, in agreement with the electronic spectra which are typical of distorted tetrahedral geometries

Furthermore the *g* values of the $(1,4\text{-MepipzH}_2)\text{CuCl}_m\text{Br}_{4-m}$ complexes are lower than those of the $(1\text{-MepipdH})_2\text{CuCl}_m\text{Br}_{4-m}$ complexes, confirming a great amount of distortion in the former complexes Magnetic moments and $\langle g\rangle$ values furthermore decrease as the bromine atom number increases

The far-infrared spectra for the complexes and for the starting amine hydrohalide salts are reported in Table IV Comparison of the vibrational spectra of the complexes with those of the hydrohalide salts show that the internal vibrations of the cations disappear on complexation or are masked by the more intense vibrations of the haloanions, for which they may not be confused with the metal–halogen stretching vibration assignments Furthermore, since

TABLE IV. Far-infrared Spectra (cm^{-1}) of the Amine Hydrohalide Salts and the Complexes in the Solid State.

	Approx. Geom.	ν(CuCl)			ν(CuBr)		Other Far-i.r. Bands (below 400 cm^{-1})					
1-MepipdHCl							346m	337m	175vs	156s	110s	78m
1-MepipdHBr							345sh	335m	224wb	164w	130s	94ms
							64m					
(1-MepipdH)$_2$CuCl$_4$	D_{2d}	290vsb	262s	230m			343m	184sh	158s	126s	75w	
(1-MepipdH)$_2$CuCl$_3$Br	C_s	294sh	281vsb	260sh	225m		342m	186w	154m	124m	70w	
(1-MepipdH)$_2$CuCl$_2$Br$_2$	C_{2v}	280vs	255sh		226m	215sh	342w	292sh	184sh	158sh	122m	70w
(1-MepipdH)$_2$CuClBr$_3$	C_s	278s			222vsb	212sh	341w	292sh	184s	160m	118ms	67w
(1-MepipdH)$_2$CuBr$_4$	D_{2d}				228s	218sh	340w	184vw	161m	121ms	96w	83w
							67w					
1,4-Mepipz(HCl)$_2$							375s	316m	268s	220sh	182vsb	160sh
							112ms	78m				
1,4-Mepipz(HBr)$_2$							373s	316m	276sh	262s	220w	144vs
							96ms					
(1,4-MepipzH$_2$)CuCl$_4$	D_{2d}	295vs	279s	231m			176s	142m	106m	89w	76w	
(1,4-MepipzH$_2$)CuCl$_3$Br	C_s	313vs	298sh	288sh	248m		176s	140sh	102m	83m		
(1,4-MepipzH$_2$)CuCl$_2$Br$_2$	C_{2v}	300sh	281vs		225mb		190sh	165m	124sh	86m		
(1,4-MepipzH$_2$)CuClBr$_3$	C_s	280vs			234m	214s	184sh	160s	142m	82m		
(1,4-MepipzH$_2$)CuBr$_4$	D_{2d}				236m	214s	175w	155w	142ms	100w	78m	

several sets of compounds of the same stereochemistry are available, the halogen varying from Cl to Br, the assignment of the metal–halogen stretching vibrations is performed with reasonable certainty.

The spectra of the tetrachlorocuprates strictly agree with that of Cs_2CuCl_4 and with other $(CuCl_4)^{2-}$ ions for which D_{2d} symmetry was unequivocally recognized [4, 9] and may be assigned analogously. The two peaks at 290–295 and 262–279 cm^{-1} may be ascribed to the isolated ion *e* stretching mode and the b_2 stretching to the band that appears at 230–231 cm^{-1}. The *e* stretching mode remains at a frequency typical of D_{2d} ions [9]. The *e* and b_2 separation is greater than for the Cs_2CuCl_4 complex, indicating a greater degree of flattening of the tetrahedron in our complexes. Furthermore the splitting of the *e* vibration in the tetrabromocuprates indicates that some distortion from D_{2d} symmetry must be present.

The far-infrared spectra of the mixed-halocuprates are interpreted on the basis of tetrahedral C_s symmetry [for which we predict three i.r.-active Cu–X and one i.r.-active Cu–Y stretching mode [21, 22]] in the case of the $(CuX_3Y)^{2-}$ anions and on the basis of tetrahedral C_{2v} symmetry [for which we predict two i.r.-active Cu–X and two i.r.-active Cu–Y stretching modes [21, 22]] in the case of the CuX_2-$Y_2)^{2-}$ anions.

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