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Spectroscopic Investigation of Tetrachlorocuprate(II) Salts of Aminopyridinium Cations

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Five substituted pyridinium tetrachlorocuprate(II) salts have been prepared and characterized. Infrared studies clearly indicate a substantial interaction between the chloro ligands and the pyridinium hydrogens as well as substituent amine hydrogens. Electronic and electron spin resonance spectra both indicate similar distortion from planar (or tetrahedral) symmetry for all five salts. A fit of D_{2d} energy levels with the three possible d–d absorption bands shows that the angle of distortion is between 65 and 67 degrees.

Introduction

The halocuprate(II) and, in particular, the tetrachlorocuprate(II) anions have been extensively investigated because of the large number of geometries they assume, ranging from square planar through trigonal bipyramidal to tetragonally distorted octahedral [1]. While most of the studies of the tetrachlorocuprates have featured alkylammonium counterions, there have been only a few reports concerning halocuprates(II) prepared with substituted pyridinium ions. One group has prepared tetrachlorocuprates(II) of the amino-substituted pyridinium ions [2] as well as other pyridinium ions [3], but has limited their studies to the infrared characterization of the pyridinium cations.

Therefore, we have initiated a study of some pyridinium salts of halocuprates(II). We report here our spectroscopic studies of five tetrachlorocuprate(II) salts with the pyridinium cations prepared from 2-aminopyridine ($2NH_2Py$), 2-amino-5-picoline ($2NH_25Pic$), 2-amino-4,6-lutidine ($2NH_24,6Lut$), 4-aminopyridine ($4NH_2Py$) and 2-picolyl chloride (2ClPic). Halocuprates(II) with related pyridinium ions will be the subject of future communications.

Experimental

The pyridinium hydrochloride salts for spectroscopic comparison were prepared by bubbling gaseous HCl into ether solutions of the pyridines. Preparation of the pyridinium tetrachlorocuprates(II) consisted of refluxing equimolar (*e.g.*, 0.04 mol) mixtures of anhydrous $CuCl_2$ and the substituted pyridine in a 100 ml mixture of concentrated hydrochloric acid and ethanol (1:1 v/v) for a two hour period. The solutions were then allowed to evaporate slowly at *ca.* 35 °C and the crystalline products which formed in a period of days were filtered off and washed with portions of anhydrous ether. All starting materials were of Reagent Grade and partial elemental analyses were performed by either Micro-Analysis of Wilmington, Delaware or Canadian Microanalytical Service of Vancouver, B.C., Canada.

The infrared spectra were recorded as nujol and hexachlorobutadiene mulls between CsBr plates with a Perkin-Elmer 287 IR Spectrometer. Mull transmission electronic spectra were obtained with a Perkin-Elmer 330 Spectrometer. Electron spin resonance spectra, calibrated using DPPH (g = 2.0036), were recorded of finely ground powders in 3 mm tubes with a Varian E-3 Spectrometer.

Results and Discussion

Shown in Table I are the partial elemental analyses for the five salts along with their powder colors and decomposition ranges. Although none of these salts show dramatic color changes with temperature variation, there are some differences in the shades of yellow at liquid nitrogen temperature, usually with the colors being more of a true yellow at the lower temperature (*i.e.*, first three compounds in Table I). Upon heating the powders all of these salts undergo decomposition with the $2ClPicH^+$ salt decomposing

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TABLE I. Colors, Partial Elemental Analyses and Decomposition Ranges of Substituted Pyridinium Tetrachlorocuprates(II).

Compound	Color	Calculated		Found		Decomposition (°C)
		C	H	C	H	
[2NH$_2$PyH]$_2$CuCl$_4$	golden yellow	30.36	3.57	30.77	3.64	142–145
[2NH$_2$5PicH]$_2$CuCl$_4$	golden yellow	34.02	4.28	33.83	4.27	142–145
[2NH$_2$4,6-LutH]$_2$CuCl$_4$	orange yellow	37.22	4.91	36.89	4.86	145–147
[4NH$_2$PyH]$_2$CuCl$_4$	yellow	29.04	3.90	28.62	3.71	193–196
				29.36	3.57	
[2ClPicH]$_2$CuCl$_4$	bright yellow	31.16	3.05	30.76	2.87	97–100

TABLE II. Infrared Assignments (cm^{-1}) for Substituted Pyridinium Tetrachlorocuprates(II).

Compound	ν_{N-H} (asym)	ν_{N-H} (sym)	ν_{pyH^+}	δ_{NH_2}	$\nu_{C=N^+}$	ν_{Cu-Cl}
2NH$_2$PyH$^+$Cl$^-$	3308s	3143s	2755m	1664s	1621s	
	3238s		2621m			
			2593m			
[2NH$_2$PyH]$_2$CuCl$_4$	3350s	3170s	2840m	1662s	1617s	281sh
	3291s		2783m			274s
			2728w			258s
			2698w			
			2620w			
2NH$_2$5PicH$^+$Cl$^-$	3335s	3155s	2758w	1665s	1627s	
	3290s		2695w			
	3250s					
[2NH$_2$5PicH]$_2$CuCl$_4$	3420s	3191s	2783w	1668s	1621s	283s,b
	3322s		2710m			277sh
	3240s		2568m			264m
			2510m			
2NH$_2$4,6-LutH$^+$Cl$^-$	3320s,b	3134s	2724m	1660s	1633s	
			2610w			
[2NH$_2$4,6-LutH]$_2$CuCl$_4$	3385s	3182s	2766w	1666s	1637s	288s
	3295s		2728m			261m
			2592m			
			2524w			
4NH$_2$PyH$^+$Cl$^-$	3313s	3143s	2968w	1650s	1609s	
	3195s	3091s	2936w	1632s		
[4NH$_2$PyH]$_2$CuCl$_4$	3385s	3209s	2870w	1656s	1600s	274sb
	3308s	3092s	2835w			259sb
			2693w			
			2656w			
2ClPicH$^+$Cl$^-$			2710w		1628m	
			2625w		1611m	
[ClPicH]$_2$CuCl$_4$			2720m		1632m	261s,vb
			2675m		1617m	

at a much lower temperature than the four aminopyridinium salts. This would seem to suggest that the amino protons, as well as the pyridinium proton, are involved in hydrogen bonding to the CuCl$_4^{2-}$ ions in these four solids. Lending credibility to this suggestion is the very similar decomposition ranges of the three 2-aminopyridinium salts suggesting a similar role for the amino hydrogens (*e.g.*, 'intraionic' hydrogen bonding). The much higher decomposition temperature for [4NH$_2$PyH]$_2$CuCl$_4$ would be consistent with an alternate form of hydrogen bonding (*e.g.* 'interionic') such as depicted in Fig. 1.

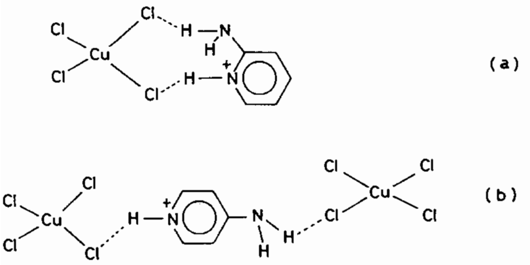

Fig. 1. A possible depiction of a) 'intraionic' hydrogen bonding and b) 'interionic' hydrogen bonding involving $CuCl_4^{2-}$.

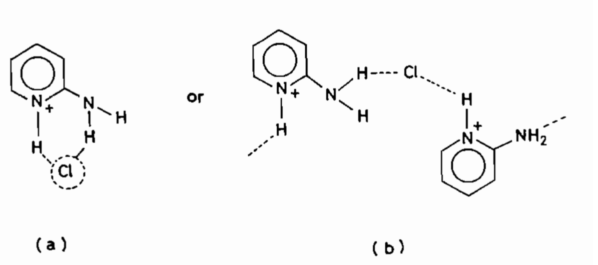

Fig. 2. A possible depiction of a) 'intraionic' hydrogen bonding and b) 'interionic' hydrogen bonding involving Cl^-.

The infrared bands which are most useful in establishing the nature of both the cation and the $CuCl_4^{2-}$ anion as well as the extent of hydrogen bonding between the two ions are tabulated in Table II. Spinner [4] has reported a compilation of the bands due to various modes for the different aminopyridines and 2-aminopicolines, as well as their hydrochlorides. His assignments for the relevant hydrochlorides (and our own for $2NH_24,6LutH^+Cl^-$ and $2ClPicH^+Cl^-$) are included in Table II. In the hydrochlorides the proton is considered to be added to the pyridine nitrogen rather than the amino group due to its higher base strength [5] and this has been confirmed by a study of the electronic [6] and infrared spectra [4].

Loss of ring electron density due to protonation of the pyridine would cause electron density to be shifted from the amine groups lowering their mean ν_{N-H} energy but raising the energy of δ_{NH_2} due to increased double bond character of the carbon–nitrogen bond. When one compares these two quantities in the spectra of the pyridinium hydrochlorides and their respective pyridines, the mean ν_{N-H} energy is decreased (*i.e.*, $2NH_2PyH^+Cl^-$, 74 cm^{-1}; $2NH_25PicH^+Cl^-$, 50 cm^{-1} and $4NH_2PyH^+Cl^-$, 88 cm^{-1}) and δ_{NH_2} is increased (*i.e.*, $2NH_2PyH^+Cl^-$, 37 cm^{-1} and $2NH_25PicH^+Cl^-$, 38 cm^{-1}) the δ_{NH_2} band being essentially unchanged upon protonation of $4NH_2Py$ [4]. Hydrogen bonding of the amine function would also cause shifts of these two bands in the same directions and a comparison of the energies of these two amino vibrations between the chloride and tetrachlorocuprate(II) salts may show the importance of this factor.

When the spectra of ammonium hydrochlorides and the corresponding ammonium tetrachlorocuprates(II) are compared, ν_{N-H} has been found to undergo a positive shift of 250–300 cm^{-1} and δ_{NH_2} to be lowered by 25–35 cm^{-1} for the tetrachlorocuprate(II) salts [7]. These shifts are reported to be due to the decreased electron density available on the chloro ligands (of $CuCl_4^{2-}$) compared to the chloride ion resulting in considerably weaker hydrogen bonding in the tetrachlorocuprate(II) salts. A comparable change would be expected for the pyridine proton of these pyridinium salts as measured by shifts in ν_{py-H^+} and $\nu_{C=N^+}$. However, inspection of the relative energies for these bands between the five pairs of salts in Table II shows that they are relatively unchanged and, except for the $2ClPicH^+$ ion, the shifts in energy are in the opposite direction to what would be expected. That is, the hydrogen bonding of the pyridinium hydrogen to the tetrachlorocuprate(II) ion is as strong, if not stronger, than to the chloride ion.

One possible explanation for this finding is that the amino groups are also participating in hydrogen bonding to the anions. The mean ν_{N-H} of the amino groups shifts to higher energies in the tetrachlorocuprate(II) salts compared to the chloride salts (*i.e.*, $2NH_2PyH^+$, 40 cm^{-1}; $2NH_25PicH^+$, 35 cm^{-1}; $2NH_24,6LutH^+$, 70 cm^{-1}; and $4NH_2PyH^+$, 63 cm^{-1}). The δ_{NH_2} mode shows little change in comparing the various pairs of salts. The changes in the mean ν_{N-H} can be accounted for by stronger hydrogen bonding by the pyridinium group to the tetrachlorocuprate(II) ion, thereby restoring electron density to the ring system and therefore, the amino group. A second factor may simply be weaker hydrogen bonding of the amino group to the tetrachlorocuprate(II) ion than the chloride ion.

Since both factors are likely to be involved, it is of interest to note that the amino group must compete to some extent in aminopyridinium salts for the electron density of the anions in order to form hydrogen bonds. In Fig. 2 we show some plausible structures for this 'competition' for the chloride ion.

This competition in hydrogen bonding in the $CuCl_4^{2-}$ salts evidently is less evenly matched because of the positive shift of the mean ν_{NH} of the amino group and the negative shift (or no change) of $\nu_{\overset{+}{py}-H}$. This is most likely due to the greater number of sites available for hydrogen bonding as well as the reduced electron density of the chlorine ligands. It should be emphasized that the aminopyridinium ions appear to bond to $CuCl_4^{2-}$ more strongly than to Cl^-, which is opposite to the situation with ammonium ions.

TABLE III. Electronic Spectra (kK) of Some Substituted Pyridinium Tetrachlorocuprates(II).

Compound	Cation ($\pi \rightarrow \pi^*$, $n \rightarrow \pi$)*	Cl(π) → Cu(d)	Near Infrared
$[2NH_2PyH]_2CuCl_4$	40.82, 31.25	25.00	9.80, 8.70, 7.19sh, 6.49sh, 5.13
$[2NH_25PicH]_2CuCl_4$	43.10, 32.79	25.00, 22.73sh	9.90, 8.90sh, 7.17sh, 5.02sh, 4.40sh
$[2NH_24,6\text{-}LutH]_2CuCl_4$	40.00, 32.26	24.63, 22.22sh	10.10, 8.40sh, 7.41sh, 5.00sh, 4.43sh
$[4NH_2PyH]_2CuCl_4$	37.88	25.06	9.73, 8.85sh, 6.78, 5.83sh, 4.82sh
$[2ClPicH]_2CuCl_4$	36.76, 33.33sh	24.45	9.71, 9.00sh, 6.79, 6.48sh

This factor may be of importance in interpreting the energies of the observed d–d bands later in this work.

Also included in Table II are our tentative assignments of the ν_{Cu-Cl} bands for the $CuCl_4^{2-}$ ions of the five salts. While the pyridinium ions do have bands in this region of the spectrum, like other authors [8], we find that these vibrations of the cations appear unshifted compared to their positions in the spectra of the chloride salts or are masked by the more intense vibrations of the $CuCl_4^{2-}$ ions.

Most tetrachlorocuprates(II) reported on to date have been found to be of D_{2d} symmetry which yields two ν_{Cu-Cl} bands (e and b_2) or three bands if the e mode is split. Other workers [8] have observed the two e stretching frequencies in the ranges 290–295 and 262–279 cm^{-1} with the b_2 stretching mode at 230–231 cm^{-1} with piperidinium and piperazinium cations. However, in the pyridinium salts reported on here, the splitting of the e mode, when resolved, is not as large and the b_2 mode occurs at about 260 cm^{-1} with no indication of a band in the 230 cm^{-1} region. For $[2ClPicH]_2CuCl_4$ only a single, very broad band was observable in its spectrum. These findings would suggest that the geometry of the $CuCl_4^{2-}$ ions in this study is something less than D_{2d} due to the more complicated nature of the hydrogen bonding involved.

Whereas most previous workers [1] were able to assign five charge transfer bands for D_{2d} $CuCl_4^{2-}$, unfortunately strong $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands due to the pyridinium ring obscure all but the lowest energy Cl(π) → Cu(d) charge transfer bands. Bands arising for both types of transitions are collected in Table III as are the lower energy d–d transitions. While no further comment is required on the bands assigned to the various cations, some brief statements about the charge transfer bands are appropriate. The low energy shoulder (*ca.* 22 kK) is difficult to assign due to the high intensity of the band at *ca.* 25.0 kK. Also, the broadness of the band at *ca.* 32 kK suggests that it owes part of its relatively high intensity to one of the ^2E components of a Cl → Cu(II) charge transfer band [10].

While most studies of the various D_{2d} $CuCl_4^{2-}$ salts have reported two bands for the d–d transitions in the spectral regions 5.8–6.4 and 8.9–9.5 kK [8, 10], D_{2d} symmetry would allow for three or even four bands (*i.e.*, when the excited ^2E level is split). We have attempted to extract the maximum number of bands from our mull transmission spectra for this series of salts. Overlapping of bands as well as combination bands of the ν_{N-H} and ν_{C-H} modes of the cations are the major difficulties in assignment.

Narrow bands in the range 6.50–6.60 kK are assignable to $2(\nu_{N-H})$ while those at *ca.* 5.0 kK are likely due to $2(\nu_{\mathrm{p\overset{+}{y}-H}})$ modes. The very low energy bands found in the spectra of the two alkyl-substituted cations are probably due to a combination band involving ν_{C-H} and $\nu_{C=C}$. Assignments of the d–d bands and a discussion of their relative energies in terms of structural properties will be deferred until later.

The powder ESR data are compiled in Table IV. All of the spectra are consistent with a $d_{x^2-y^2}$ (or d_{xy}) ground state for the $CuCl_4^{2-}$ ions and the $g_\parallel$ values are in the range reported for other D_{2d} $CuCl_4^{2-}$ ions [8, 11]. Upon cooling, $g_\parallel$ (and $g_\perp$) is shifted in all the complexes. A shift toward the free spin value is indicative of movement of the $CuCl_4^{2-}$ toward a more planar geometry. It is interesting that the two larger cations of the series show a decrease in $g_\parallel$ with cooling; the only planar $CuCl_4^{2-}$ ions are found with very large cations [12] or with cations capable of forming very strong hydrogen bonds. The positive shifts in $g_\parallel$ for the remaining three salts indicate that they assume a more tetrahedral structure at the lower temperature.

Our assignments of the ν(d–d) bands to the D_{2d} levels $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions are included in Table V. A number of different proposals have been made for correlating the energy of the d–d transitions with a distortion parameter

TABLE IV. ESR Parameters Derived from Powders of Substituted Pyridinium Tetrachlorocuprates(II).

Compound	298 K			77 K		
	$g_{\parallel}$	$g_{\perp}$	g_{ave}	$g_{\parallel}$	$g_{\perp}$	g_{ave}
$[2NH_2PyH]_2CuCl_4$	2.371	2.098	2.189	2.405	2.088	2.194
$[2NH_2PicH]_2CuCl_4$	2.329	2.064	2.152	2.316	2.062	2.147
$[2NH_24,6\text{-}LutH]_2CuCl_4$	2.351	2.070	2.164	2.338	2.062	2.154
$[4NH_2PyH]_2CuCl_4$	2.315	2.081	2.159	2.372	2.069	2.170
$[2ClPicH]_2CuCl_4$	2.367	2.077	2.174	2.386	2.065	2.172

TABLE V. d–d Transition Assignments (kK) and Covalency Parameters for Some Tetrachlorocuprates.

Cation	Symmetry	$^2B_2 \rightarrow {}^2A_1$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2E$	$g_{\parallel}$	$g_{\perp}$	$k_{\parallel}^2$	$k_{\perp}^2$	References
Cs^+	D_{2d}	9.05	7.90	5.55 4.80	2.384	2.105 2.083	0.455	0.287	[15]
$2NH_2Py^+$	?	9.80	8.90	7.19	2.371	2.098	0.495	0.415	This work
$2ClPicH^+$	?	9.71	9.00	6.79 6.48	2.367	2.077	0.495	0.299	This work
$2NH_24,6Luth^+$	?	10.10	8.40	7.41	2.351	2.070	0.442	0.303	This work
$QuinH_2^{2+}$	?	10.10	8.49^b	6.85^b	2.346	2.104	0.440^a	0.420^a	[11]
$2NH_25PicH^+$	?	9.90	8.90	7.17	2.329	2.064	0.438	0.267	This work
$4NH_2PyH^+$	?	9.73	8.85	6.78	2.315	2.081	0.417	0.322	This work
$1,4MpipzH_2^{2+}$	?	9.43	8.86^b	6.33	2.313	2.094^b	0.415^a	0.350^a	[8]
		$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2B_{2g}$					
$N\text{–}mph^+$	D_{4h}	16.13	13.70	11.76	2.221	2.040	0.388	0.311	[12]

[a] Estimated. [b] Calculated. [c] J. Ferguson, *J. Chem. Phys., 40,* 3406 (1964).

[13, 14]. Both of the above proposals involved the highest energy d–d band and were reasonably successful in showing a meaningful trend. More recently at least two spectral bands have been reported for the D_{2d} $CuCl_4^{2-}$ salts being studied [8]. As mentioned previously, we have attempted to assign three bands in our spectra with the knowledge that the $^2B_1$ and $2A_1$ levels are not split by a large amount, the splitting decreasing with approach to pure tetrahedral symmetry. These assignments are shown in Table V. It should be noted that splitting of the ^2E level is not expected to be much greater than 0.5 kK for chlorocuprates but we tentatively assign the two components for two of the salts we have studied. We have included the results of other authors when at least two d–d bands have been assigned and the powder ESR spectral parameters have been reported. The order of listing the compounds in Table V is based on their powder $g_{\parallel}$ value in that its assignment can be made more accurately than $^2B_2 \rightarrow {}^2A_1$.

The g-values are included in Table V and they have been employed in the calculation of the covalency parameters from the following expressions:

$$k_{\parallel}^2 = \frac{(g_{\parallel} - 2.0023)E(^2B_1 - {}^2B_2)}{8\lambda}$$

and

$$k_{\perp}^2 = \frac{(g_{\perp} - 2.0023)E(^2E - {}^2B_2)}{2\lambda}$$

in order to evaluate the assignments of $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$. The spin orbit coupling parameter λ has the value 0.828 kK for Cu(II). Other than Cs_2CuCl_4, which is known to be less distorted from pure tetrahedral symmetry than the ammonium salts, there appears to be a regular trend in values for $k_{\parallel}^2$, but no trend for $k_{\perp}^2$. The irregularity of Cs_2CuCl_4 probably relates to the lack of hydrogen bonding in this salt making its copper–chlorine bonding somewhat more covalent, as well as more tetrahedral

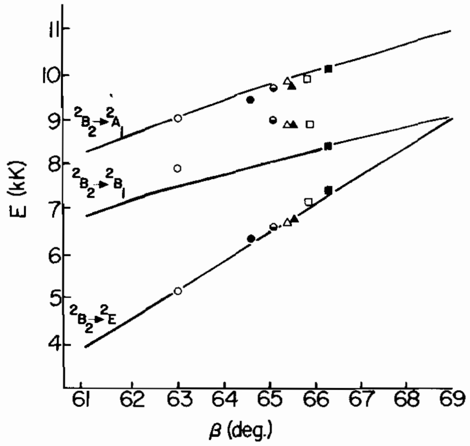

Fig. 3. A plot of d–d band energies (kK) *versus* the distortion angle (β) for various tetrachlorocuprate(II) salts. (○ = Cs$^+$, ● = 1,4MpipzH$_2^{2+}$, ◒ = 2ClPicH$^+$, △ = ZNH$_2$PyH$^+$, ▲ = 4NH$_2$PyH$^+$, □ = 2NH$_2$5PicH$^+$, and ■ = 2NH$_2$4,6LutH$^+$).

[14]. The apparent trend in $k_\parallel^2$ values gives credibility to our assignments of the $^2B_2 \to {}^2B_1$ bands and this prompted us to attempt to fit our experimental data with more extensive theoretical calculations involving the three bands expected for D_{2d} symmetry. Recently a report of such an attempt with a few tetrachlorocuprates (II) has been communicated in which the authors then extended their calculations to CuS_4 chromophores [16]. The crystal field equations first reported by Piper and Hatfield [17] were employed.

Six compounds from Table V are included in Fig. 3 and there is excellent agreement between the calculated energy levels $^2B_2 \to {}^2A_1$ and $^2B_2 \to {}^2E$ and the experimental points. Based on this fit it would appear that the angle of deviation from the orthogonal line through the copper center, β, is between 65 and 67° for the five compounds of this study. The fit to the line for $^2B_2 \to {}^2B_1$ is very poor except for the 2-aminolutidine salt which fits surprisingly well. Although not all three energy levels are fit, such a plot does show that a mull transmission electronic spectrum can be quickly recorded on a new material allowing the researcher the opportunity to evaluate the distortion of the $CuCl_4^{2-}$ chromophore (or other Cu(II) chromophores). This fitting, or lack of, may aid in the decision concerning the need for a crystal structure study.

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