

Spectral and Thermal Studies of Tetrachlorocobaltate(II) Salts of Aminopyridinium Cations

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Tetrachlorocuprate(II) salts have been extensively investigated because of the structural variations that the Cu(II) center achieves depending on the nature of the cation [1]. Although the alkylammonium salts have received the greatest attention, aminopyridinium chlorocuprates have recently been studied spectroscopically [2] and magnetically [3]. In a study of acetylpyridinium chlorometallates we prepared and characterized the three chlorocobaltates [3]. Although there was extensive variation in the nature of the chloronickelate(II) and chlorocuprate(II) salts, the three chlorocobaltate(II) salts had similar spectral properties.

The quinolinium salt of CoCl_4^{2-} has been spectrally characterized [5], but pyridinium salts have not, to our knowledge, been investigated. However, crystal structures of a number of CoCl_4^{2-} salts with alkylammonium counterions have been communicated [6]. The anion has been shown to have a distorted tetrahedral coordination geometry in each of these salts, but the nature of these distortions does not follow a recognizable trend because both hydrogen bonding and electrostatic crystal effects influence the distortion [6]. We report here the spectral and thermal characterization of a series of aminopyridinium and 2-aminopicolinium tetrachlorocobaltates(II).

The compounds were prepared by refluxing a 2:1 molar ratio of substituted pyridine with CoCl_2 in a mixture of concentrated HCl and ethanol (1:1 by volume). Slow evaporation of the solutions yielded blue crystalline products which were then recrystallized from absolute ethanol. Partial elemental analyses by Micro-Analysis of Wilmington, Del., confirmed the composition of the products. Plasma desorption mass spectra of three of the solids were obtained at the National Institutes of Health as described elsewhere [7], and the spectral and thermal data were obtained as described in previous reports from this laboratory [4, 8]. With the excep-

tion of the solid derived from $3\text{NH}_2\text{PyH}^{+**}$, which apparently consists of three monovalent cations and a chloride ion as well as a tetrachlorocobaltate(II) anion, the remaining compounds are the expected 2:1 salts or pyridinium cations and CoCl_4^{2-} .

There is considerable variation in the melting points of the compounds listed in Table I, with the highest being found for the most highly substituted cation, $2\text{NH}_2,4,6\text{LutH}^+$. Assuming that the melting point is related to the strength and extent of hydrogen bonding, this compound would appear to have the strongest hydrogen bonding to the coordinated chloride ions. The greater size of this ion may cause a more tightly packed crystal, and therefore allow for stronger hydrogen bonding. Further speculation on the relative melting points of the compounds seems unjustified except to note the following: the melting points of the products with 3- and 5-substituted cations are the lowest of the series. This suggests that the inductive effect of the amino and methyl substituents is a significant factor.



Also included in Table I are the enthalpy data obtained by differential scanning calorimetry, along with mass spectral data for three of the solids. For comparison, the enthalpies of fusion for the 2-, 3- and 4-acetylpyridinium tetrachlorocobaltates(II) were determined to be 8.9, 7.2 and 7.6 kcal/mol, respectively [4]. The order of the enthalpies of fusion for the aminopyridinium salts is identical (*i.e.*, 2- > 4- > 3-substituted), suggesting that the position of a substituent on the ring may be the dominant factor in the strength of the electrostatic interaction of the cation. Since amino and acetyl groups have opposite inductive effects on a ring's electron density, their steric contributions must be more important than their electronic effects. Further, this suggests that the involvement of the amino group in hydrogen bonding is unimportant, since the enthalpy values of these compounds are similar to those of the series of pyridinium ions.

The relative contribution to fusion enthalpy, following the order 2- > 4- > 3-substituted, is observed also in the series of 2-aminopicolinium compounds. The 2-amino-6-picolinium salt has a value higher than that of the unsubstituted 2-aminopyridinium salt. The 4-picolinium salt also has a higher value than does the unsubstituted solid. The order $2\text{NH}_2,4,6\text{LutH}^+ > 2\text{NH}_2,6\text{PicH}^+ > 2\text{NH}_2,4\text{PicH}^+ > 2\text{NH}_2\text{PyH}^+$ fits this steric factor relationship. Since 3-substitution gives the lowest enthalpy value in both the acetyl- and aminopyridinium series, the order $2\text{NH}_2,3\text{PicH}^+ < 2\text{NH}_2\text{PyH}^+$ is also as expected. The

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**Symbols such as $3\text{NH}_2\text{PyH}^+$, which represents the 3-aminopyridinium ion, are used throughout this communication.

TABLE I. Thermal and Mass Spectral Data for Aminopyridinium Tetrachlorocobaltates(II)

Compound	Melting point (°C)	DSC		Cation (<i>m/z</i>)	
		Endotherms (°C)	ΔH (kcal mol ⁻¹)		
[2NH ₂ PyH] ₂ [CoCl ₄]	170–172	118 weak 133 weak 173 strong, sharp	1.83 2.45 4.03	8.31	
[3NH ₂ PyH] ₃ [CoCl ₄]Cl	156–158	134 (141 sharp) weak 170 strong	2.49 3.93		6.42
[4NH ₂ PyH] ₂ [CoCl ₄]	194–198	190 broad	8.05	95(4NH ₂ PyH ⁺)	
[2NH ₂ 3PicH] ₂ [CoCl ₄]	168–170	134 (125 sharp) medium 170 strong	1.72 3.64	5.36	109(2NH ₂ 3PicH ⁺)
[2NH ₂ 4PicH] ₂ [CoCl ₄]	165–166	164 strong, sharp	8.76		92 ()
[2NH ₂ 5PicH] ₂ [CoCl ₄]	138–142	140 broad	14.23	109(2NH ₂ 4PicH ⁺)	
[2NH ₂ 6PicH] ₂ [CoCl ₄]	180–182	180 strong, sharp	9.28	92 ()	
[2NH ₄ 4,6LutH] ₂ [CoCl ₄]	230–232	229 (232 sharp) strong, sharp	12.50		

weaker DSC peaks at temperatures below the melting points may represent partial breaking of the hydrogen bonded lattice.

The negative ion mass spectra are identical for the three solids (see Table I) with no primary peak assignable to CoCl₄²⁻. However, the decomposition species CoCl₃⁻ and the recombination product Co₂-Cl₅⁻ are observed with the expected isotopic peaks, confirming the presence of CoCl₄²⁻ ions [7]. The positive ion mass spectra show peaks for the parent pyridinium cations as well as secondary peaks for the two 2-aminopicolinium salts at *m/e* = 92 due to loss of NH₃.

There is little variation in the energy maxima for ν_2 (6.13–6.41 kK) and ν_3 (14.93–15.15 kK) for this series of solids. The average of these gives approximate values of 700 cm⁻¹ and 350 cm⁻¹ for *B* and *Dq*, respectively, which are similar to values found for the salts of the acetylpyridinium ions [4] and quinolinium ion [5]. However, our value of *B* is lower than the 745 cm⁻¹ found for the larger cinchoninium tetrachlorocobaltate(II) [9], indicating more covalent Co–Cl bonds in our compounds. This greater covalency probably arises from stronger hydrogen bonding [9, 10], to the smaller pyridinium cations, allowing more π -character in the Co–Cl bonds.

All solids show a strong, broad band at *ca.* 300 cm⁻¹, and any structural variations that occur in the series are insufficient to significantly alter this band's nature. Both $\nu(\text{NH}_2)$ bands of the amino groups are

30–70 cm⁻¹ higher in energy in the spectra of the CoCl₄²⁻ salts compared to those of the corresponding chlorides [11]. A similar result was found for the CuCl₄²⁻ salts [2], which indicates that the greater electron density of the smaller Cl⁻ ion promotes stronger hydrogen bonding in both series. The $\nu(\text{NH})$ multiplet assignable to the pyridinium nitrogen in the CoCl₄²⁻ salts is at higher energy (40–80 cm⁻¹) than in the spectra of the corresponding CuCl₄²⁻ salts, indicating much weaker hydrogen bonding to CoCl₄²⁻. The strong hydrogen bonding of CuCl₄²⁻ is accompanied by distortion from tetrahedral towards square planar symmetry and results in an approximate *D_{2d}* symmetry. The lack of plasticity of a Co(II) center compared to a Cu(II) presumably prevents distortion, as was also shown for cyclohexylammonium tetrachlorocobaltate(II) [6], and therefore does not allow for the hydrogen bonding to be as strong.

In conclusion only the thermal results show differences between the various CoCl₄²⁻ centers of this study, and these differences appear to be due to steric effects rather than differences in hydrogen bonding.

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