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Structural consequences of M-Cl···H-N hydrogen bonds in substituted pyridinium salts of the cobalt(II)tetrachloride anion isolated from liquid clathrate media

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The crystal and molecular structures of two substituted pyridinium salts of the cobalt(II)tetrachloride anion, [4-picolinium]$_2$[CoCl$_4$] 1 and [4,4'-Bipyridinium][CoCl$_4$] 2, isolated from liquid clathrate media are reported in order to gain an understanding into the preferred orientation adopted by such interacting moieties. We demonstrate that M-Cl···H-N hydrogen bonds principally govern the solid-state self-assembly of these systems. Furthermore, we reveal that 1 possesses the first noted example of a dimeric three-center hydrogen bond.

The importance of hydrogen bonding interactions in controlling the self-assembly of molecules and ions in the solid-state has been recognized.[1] Indeed, the structural effects of hydrogen bonding in organic crystals has been extensively studied with a number of preferred patterns identified.[2] For example, Etter *et al.* have outlined general guidelines describing the solid-state organization exhibited by functional groups such as amides, diaryl ureas and imides.[2d] Recently, however, there has been a surge of interest in understanding the nature and structural manifestations of hydrogen bonding in coordination chemistry.[3] Specifically, the factors affecting the strength[3a] and geometry[3b] of M-X···H-N hydrogen bonds have been investigated in order to extend the ideas of molecular recognition to metal-containing systems. Owing to their importance in chemical and biological processes,[4] an understanding of the structural effects and geometrical criteria of hydrogen bonds associated with metal complexes remains a desirable goal.

Extensive work by ourselves and others has focused upon the formation of two-phase liquid clathrate systems resulting from the interaction between a wide range of salts with aromatic solvents.[5] In particular, we have reported the formation of one- and two-dimensional solid-state hydrogen bond networks composed of proton cryptate and oxonium ion crown ether complexes of inorganic anions isolated from such liquid clathrate media. As a result, we have gained a considerable amount of information concerning the interaction of the oxonium ion and its higher hydrated species (*i.e.* $H_3O^+(H_2O)_n$) with a variety of inorganic anions. In this contribution we report an extension of this work by using substituted pyridinium cations as hydrogen bond donors. It is hoped that these studies will fill the noted[3b] paucity of crystallographic data of these systems and thereby lend insight into the preferred orientation adopted by such interacting moieties. Herein we report the crystal and molecular structures of [4-picolinium] 2 [CoCl$_4$] 1 and [4,4'-bipyridinium][CoCl$_4$] 2 generated from liquid clathrate media. We reveal that 1 possesses the first noted example of a dimeric three-center hydrogen bond.[6] The three-center hydrogen bond plays an important role in biochemistry with its structural role in DNA being a representative example.[4,7]

Addition of anhydrous $HCl_{(g)}$ to a toluene solution (30 mL) of 18-crown-6 (1.32 g, 5 mmol), water (0.09 mL, 5 mmol) and either 4-picoline (0.93 g, 10 mmol) or 4,4'-bipyridine (0.78 g, 5 mmol) in the presence of $CoCl_2{\cdot}6H_2O$ immediately yielded a two-phase liquid clathrate solution and subsequently blue and blue-green precipitates, respectively, from the bottom layer over a period of ten minutes. The formulations of 1 and 2 were confirmed using single crystal X-ray diffraction.[8]

The X-ray crystal structure of 1 is given in Figure 1. The structure consists of two independent 4-picolinium cations and a single $[CoCl_4]^{2-}$ anion linked together by

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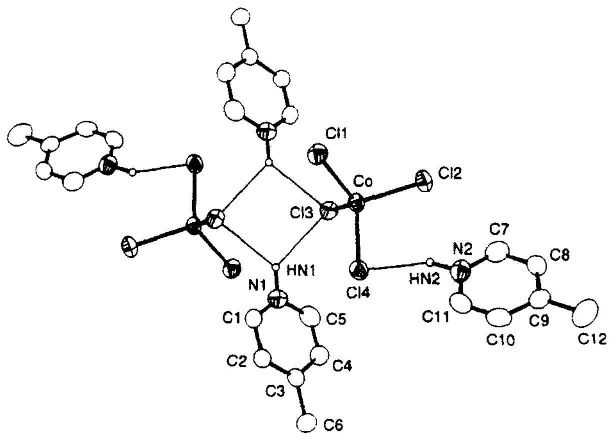

Figure 1 ORTEP perspective of the dimeric assembly of **1**.

M-Cl···H-N hydrogen bonds. Two different types of hydrogen bonds are found: a conventional two-center hydrogen bond (*i.e.* A···H-D) between C14 and N2 and a dimeric three-center hydrogen bond between Cl3 and N1. Cl···H-N and Cl···N contacts are presented in Table 1. The Cl···H-N and Cl···N distances are 2.252(1), 2.554(1) and 2.583(1), and 3.203(4), 3.353(4) and 3.296(4) Å, respectively. These Cl···N distances fall within the range of conventional two-center hydrogen bonds which typically range from 2.91 to 3.52 Å.[4] The remaining Cl···H-N contacts are greater than 2.85 Å and are not structure determining. In addition, no appreciably strong C-H···Cl or π-π interactions are present.

The X-ray crystal structure of **1**, to our knowledge, contains the first noted example of a *dimeric* three-center hydrogen bond. The 4-picolinium cation inherently possesses the ability to approach the $[CoCl_4]^{2-}$ anion without steric hinderence and is therefore able to share its NH proton between two hydrogen bond acceptors. In this case each NH proton is being shared between the same two anions around a center of inversion. The Cl···H-N distances of 2.554(1) and 2.583(1) Å indicate that the protons are equidistant from each chloride ligand. Unlike 2,6-diphenylpyridinium tetrachloroaurate,[3b] the N-H···Cl angles, 134.0(2) and 126.0(2)°, are approximately equal suggesting that the NH protons are being shared equally by both anions.[9] The Co-Cl3-HN1 angles are 91.39(4)° and 100.48(5)° while the H-Cl-H angle completing the rectangular four-atom arrangement is 82.71(3)°. The NH protons lie 0.15 Å out of the plane defined by N1, Cl3, and Cl3a which contrasts the upper limit of 0.20 Å observed in N-H(CO)X three-center hydrogen bond systems.[6] That the 4-picolinium cation engages in a three-center hydrogen bond may be attributed to a deficiency in hydrogen bond donors causing the NH proton to be shared by two hydrogen bond acceptors.[4,6]

Table 1 Interionic M-Cl...H-N Hydrogen Bond Distances (Å) and Angles (°) for **1** and **2**.

Cpd	*D*	*A*	*N...Cl*	*Cl...H*	*N-H...Cl*
1	N1	C13	3.296(4), 3.353(4)[a]	2.583(1), 2.554(1)[a]	126.0(2), 134.0(2)[a]
	N2	C14	3.203(4)	2.252(1)	152.8(3)
2	N1	C11	3.118(3)	2.135(1)	158.9(2)
	N2	C12	3.354(2)[b]	2.489(1)[b]	141.2(2)[b]

[a]N-H...C13a a: 0.500-x 0.500-y 1.000-z [b]N-H...Cl2h h: −1.000-x 1.000-y 1.000-z

Incorporation of two hydrogen bond donors within the same cation by using $[H_2bipy]^{2+}$ results in the formation of a discrete solid-state cyclic 2 + 2 structure **2** linked together by two-center M-Cl···H-N hydrogen bonds to the $[CoCl_4]^{2-}$ anion (Figure 2). The Cl···H-N contacts, Cl1···HN1 2.135(1) and Cl2h···HN2 2.489(1) Å, indicate significant hydrogen bonding interactions between the anions and the NH protons (Table 1). The N1-HN1-Cl1 and N2-HN2-Cl2h angles are 158.9(2) and 141.2(2)°, respectively. In addition, two strong C-H···Cl[10] hydrogen bonds (C2···Cl3 3.422(3), C4···Cl4 3.442(3) Å) are observed to cross-link each cyclic structure into a complex three-dimensional network. As in 1-ethyl-3-methylimidazolium tetrachlorocobaltate,[11] all of the chlorine atoms of the anion are involved in hydrogen bonding interactions. The least-squares best planes of the two pyridinium rings of the dication are approximately planar being inclined at an angle of 6.7(1)° to each other. This value compares favorably to the paraquat salts of $[CoCl_4]^{2-}$ and $[CuCl_2]_n^{n-}$ anions which are planar within experimental error but contrasts to that of the paraquat $[PdCl_4]^{2-}$ salt in which the aromatic rings are inclined 50° to each other.[12] The dications in **2** are arranged in an offset π-π stacking geometry.[13]

The $[CoCl_4]^{2-}$ anions in **1** and **2** are approximately tetrahedral with a mean Co-Cl length of 2.272(1) Å in both structures (Table 2). This value is in good agreement with those reported in the literature.[11,14] The longest Co-Cl bond lengths involve the chloride ligands engaged in M-X···H-N hydrogen bonds. It has been pointed out[11,14] that hydrogen bonding may be among the factors which determine a deviation from T_d symmetry in the $[CoCl_4]^{2-}$ anion. Although more crystallographic data are required to make this claim statistically significant,[11] it is interesting to note that the chlorine atom of the

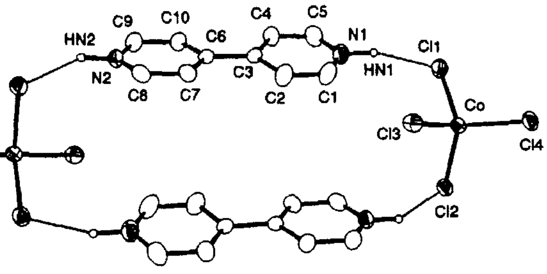

Figure 2 ORTEP perspective of the 2 + 2 structure of **2**.

Table 2 $[CoCl_4]^{2-}$ Bond Distances (Å) and Angles (°) for **1** and **2**.

		1	**2**
Distances	Co-C11	2.259(1)	2.2881(7)
	Co-C12	2.266(1)	2.289(1)
	Co-C13	2.273(1)	2.252(1)
	Co-C14	2.290(2)	2.2572(8)
Angles	C11-Co-C12	110.15(5)	111.20(3)
	C11-Co-C13	109.57(5)	107.17(4)
	C11-Co-C14	112.81(5)	110.51(3)
	C12-Co-C13	111.14(5)	106.67(4)
	C12-Co-C14	105.54(5)	111.07(4)
	C13-Co-C14	107.56(5)	110.07(4)

shorter Co-Cl3 bond in **1** is involved in the three-center hydrogen bond perhaps reflecting a weaker interaction[7] compared to the conventional two-center hydrogen bond analog.

Our preliminary results reveal that the proton rich liquid clathrate medium is a suitable solvent for the generation of these salts. Information concerning the role and nature of cation-anion interactions in these systems has been gained. These results may bear relevance for the design of hydrogen bonding ligands or multi-dimensional hydrogen bonded scaffolds where the concepts of molecular recognition are now being applied to coordination chemistry.

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SUPPLEMENTARY MATERIAL AVAILABLE

Crystallographic report, tables of positional and thermal parameters, bond lengths and angles (10 pages); tables of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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8 Samples suitable for X-ray crystallographic analysis were obtained by injecting approximately 2 mL of the liquid clathrate into 10 mL of hot, concentrated HCl and allowing the solution to cool to room temperature. Crystal data for **1**: monoclinic space group C2/c with a = 17.7305(16) Å, b = 7.760(3) Å, c = 25.3980(20) Å, β = 99.327(8)°, V = 3448.3(14) $Å^3$, D_{calc} = 1.50 g cm^{-3}, and Z = 8. Data were collected at 298 K, and the structure was refined to R_f = 0.033, R_w = 0.042 for 1836 reflections with $I > 3.0\sigma(I_{net})$. Crystal data for **2**: monoclinic space group $P2_1/c$ with a = 7.6405(14) Å, b = 19.7967(15) Å, c = 9.571(5) Å, β = 108.37(3)°, V = 1373.8(7) $Å^3$, D_{calc} = 1.73 g cm^{-3}, and Z = 4. Data were collected at 298 K, and the structure was refined to R_f = 0.026, R_w = 0.035 for 2089 reflections with $I > 3.0\sigma(I_{net})$. The NH proton hydrogen bond geometry in both structures was normalized by fixing the N-H bond distance to 1.03 Å.[6] A full description of each structure is provided in the supplementary material.

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