

A Three-Center Hydrogen Bond in 2,6-Diphenylpyridinium Tetrachloroaurate

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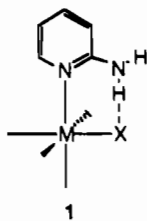
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An unusual three-center N–H···Cl₂Au hydrogen bond is present in the solid state in the title complex, which was characterized by elemental analysis and IR and ¹H NMR spectroscopy. The crystal and molecular structure has been determined by a single-crystal X-ray analysis. The compound crystallizes in the space group *P*1̄ with *a* = 9.380(2) Å, *b* = 10.219(3) Å, *c* = 11.678(4) Å, α = 89.33(2)°, β = 68.85(2)°, and γ = 64.67(2)°. Mo Kα radiation was used. The data suggest that M–Cl···H angles of ca. 90° are favorable for H-bonding, which is ascribed to the greater basicity of p-type lone pairs versus sp-type. The possibility of synthesizing hydrogen halide complexes is discussed.

Introduction

We are currently studying the structural and chemical consequences of hydrogen bonding¹ in metal complexes in the hope of applying the ideas of molecular recognition to metal complexes and catalysis. Richmond² has recently drawn attention to the facility with which fluoride complexes can H-bond, and Caulton³ has discussed H-bonding of the M–Hal group in relation to M–Hal π-bonding. To design organic molecules capable of recognizing typical substructures in metal complexes, we need to know the preferred hydrogen-bonding parameters for common types of H-bond interactions involving metal complexes. Although H-bonding interactions are of modest strength, normally in the range of 2–10 kcal/mol, they could in principle cause large alterations in rates and equilibria of reactions involving complexes. The structural aspects of H-bonding in crystals has been studied.⁴ Recent work^{5,6} has shown that strong⁶ (5–7 kcal/mol) hydrogen bonds can be formed between the amino group of 2-aminopyridine and the X group of an adjacent M–X bond, where X is F, Cl, and even H. The conformation of this system imposes a side-on approach of the N–H to the M–X bond, where the M–X···HN angle is necessarily bent (~140°), as shown in diagram 1. In order to



design better hydrogen-bonding ligands, we need to know the preferred M–X···HN angle for a variety of X groups. We have

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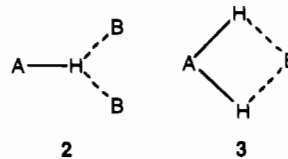
[®] Abstract published in *Advance ACS Abstracts*, May 15, 1995.

- (1) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer Verlag: Berlin, 1994.
- (2) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.
- (3) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.
- (4) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532.
- (5) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356.
- (6) Lee, J. C.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014.

therefore begun to study cases in which the hydrogen bond donor is free to approach the M–X bond at any angle.

In this paper, we look at the case of the M–Cl bond as H-bond acceptor. To maximize the interaction we have used [AuCl₄][−], a sterically unencumbered anionic complex. As its H-bond partner, we use 2,6-diphenylpyridinium ion. This cation is relatively acidic, which is expected to lead to strong H-bonding, but it is sterically encumbered so as to prevent direct binding of the unprotonated form to the metal or approach of the NH bond to the metal along the out-of-plane direction. As shown in this paper, a rare 3-center H-bond (**2**) is formed in this system having M–Cl–H angles very close to 90°. N–H···Cl–M H-bonds have previously been observed several times,^{7,8} but they have only been of the conventional 2-center (A–H···B) type. The first example⁷ seems to have been *trans*-[PtCl₂(NH₃)₂], with a Cl···N distance of 3.41 Å and a Pt–Cl···N angle of 78°. The best characterized example, using neutron diffraction at 20 K, is undoubtedly [NPr₄]₂[PtCl₄][PtCl₂(NH₂-Me)₂], with a Cl···N distance of 3.27 Å and a Pt–Cl···N angle of 78.4°.⁸

Three-center (**2**) and bifurcated (**3**) hydrogen bonds are known¹ to play important roles in biochemistry but do not seem to be widely recognized in coordination chemistry. In diagrams **2** and **3**, A–H represents the weak acid or H-bond donor and B represents the weak base or hydrogen bond acceptor.⁹



Results and Discussion

Synthesis. 2,6-Diphenylpyridinium tetrachloroaurate (**3**) was synthesized by addition of the amine to an acidic (pH = 2) solution of potassium tetrachloroaurate. The resulting salt was crystallized from the reaction mixture by evaporation and recrystallized from THF/toluene in 57% yield.

Spectroscopic Data. IR and NMR data suggests that complex **3** indeed contained both the 2,6-diphenylpyridinium

- (7) Milburn, G. H. W.; Truter, M. R. *J. Chem. Soc. A* **1966**, 1609.
- (8) Brammer, L.; Charnock, J. M.; Goggin, P. L.; Goodfellow, R. J.; Orpen, A. G.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1789.
- (9) Fritsch, V.; Westhof, E. *J. Am. Chem. Soc.* **1991**, *113*, 8271.

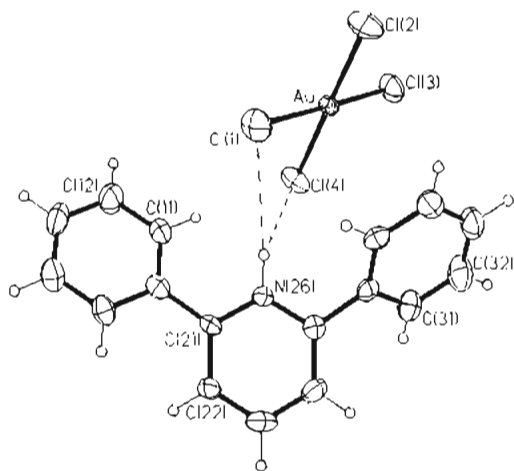


Figure 1. Structure of complex 4 with atom labels.

and tetrachloroaurate ions. In particular, the proton NMR (CD_3CN) shows a broad NH resonance at δ 14.5, as well as aromatic resonances appropriate for the diphenylpyridinium ion. The IR spectrum (Nujol) shows a band at 2975 cm^{-1} which shifts to 2403 cm^{-1} on deuteration of the pyridinium ion and so can be attributed to $\nu(\text{NH}_2\text{D})$.

Structural Studies. A suitable crystal of **3** was grown from THF/toluene and studied crystallographically. The results (Figures 1 and 2 and Tables 1–3) show the substituted pyridinium cation and the tetrachloroaurate anion, as expected, but the complex contains a rare 3-center H-bond in which the N–H is within H-bonding distance of two *cis*-chloride ligands. The sum of the Allinger van der Waals radii¹⁰ for N and Cl is 3.65 \AA , and the $\text{N}(26)\cdots\text{Cl}$ distances are 3.45 \AA [Cl(4)] and 3.75 \AA [Cl(1)]. Conventional 2-center $\text{N}-\text{H}\cdots\text{Cl}^-$ H-bonds can be much shorter than this (typical range: $2.91\text{--}3.52\text{ \AA}$),¹ but in our case we have a 3-center bond in which the distances always tend to be slightly longer and we are dealing with a neutral halo substituent and not the free Cl^- ions most often found in literature structures.¹

The proton of the pyridinium cation was located in a reasonable position in the refinement, but in any case the heavy-atom positions leave no doubt as to its location. The H-bonding hydrogen was normalized to $\text{N}-\text{H} = 1.03\text{ \AA}$ according to the standard protocol.¹ In the discussion we will use normalized coordinates, distances, and angles and use the label H_c to indicate this position and H_n to indicate the refined X-ray position. Errors in distances and angles involving H_n are difficult to estimate but may be $\pm 0.08\text{ \AA}$ and $\pm 3^\circ$. The $\text{Cl}\cdots\text{H}_n\cdots\text{N}$ distances of $2.75\text{--}(8)$ ($\text{H}_n(26\text{A})\cdots\text{Cl}(4)$) and $2.75(8)\text{ \AA}$ ($\text{H}_n(26\text{A})\cdots\text{Cl}(1)$) indicate that the NH proton is equidistant from each chloride ligand. The $\text{Au}-\text{Cl}-\text{H}_n(26\text{A})$ angles of $90(3)^\circ$ (Cl(4)) and $90(3)^\circ$ (Cl(1)) are also equal. The $\text{N}-\text{H}_n\cdots\text{Cl}$ angles, $162.7(3)^\circ$ for Cl(1) and $128.2(3)^\circ$ for Cl(4), suggest that the N–H bond dipole is aligned to point more toward Cl(1) than Cl(4), but this asymmetry could very easily be a result of packing forces, because the situation requires that this angle is strongly influenced by the packing of the bulky phenyl rings. Apart from the symmetric placement of $\text{H}_n(26\text{a})$ relative to the two chloride ligands, another criterion¹ for a 3-center H-bond is that the H-bonding proton be no more than 0.2 \AA away from the plane of the three atoms to which it is bound; in this case $\text{H}_n(26\text{a})$ is 0.013 \AA from the $\text{N}(26)\text{Cl}(1)\text{Cl}(4)$ plane.

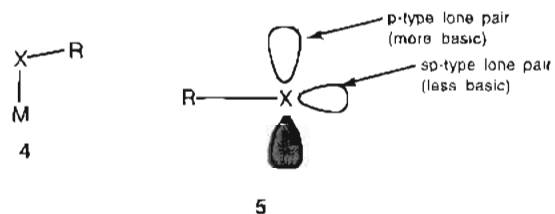
The Au–Cl bonds taking part in the H-bond are significantly elongated relative to those which are free. The average Au–Cl distance of the H-bonded Cl atoms is $2.284(3)\text{ \AA}$ versus

$2.268(4)\text{ \AA}$ for the free Au–Cl bonds. In the absence of a neutron diffraction structure it is unsafe to rely on the NH distance.

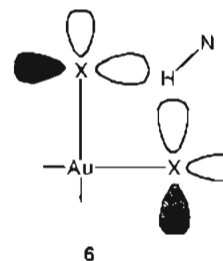
Three-Center H-Bonds. Three-center H-bonds are uncommon in metal complexes, and the factors that lead to their stability do not seem to have been discussed. In general,¹ they are known to be formed in proton-deficient structures like **3**; this complex is also a cation–anion pair, and this might give increased stability. The two Cl lone pairs, each of which would be capable of forming an H-bond independently, are directed into the same region of space, and the cation-to-anion stoichiometry of the system dictates that only one N–H is available as an H-bonding partner, but this NH bond has a choice between lying out of the square plane of the complex and H-bonding to one chloride ion or of lying closer the plane and bonding to two chlorides. The latter is clearly favored, but we do not yet know if this is because the H-bond interaction itself is stronger in a three-center system or if crystal packing forces or steric effects involving the bulky cation are responsible.

Angular Preference in $\text{M}-\text{Cl}\cdots\text{HN}$ Hydrogen Bonds. We had hoped to find the angular preference for a completely unconstrained $\text{M}-\text{Cl}\cdots\text{HN}$ system. The results indicate that the observed *ca.* 90° $\text{M}-\text{Cl}\cdots\text{H}$ angles are favorable for H-bonding, but the system is not entirely unconstrained as a result of the three-center H-bond.

An $\text{M}-\text{Cl}\cdots\text{H}$ angle close to 90° was expected because our previous work on halocarbon complexes of type **4** showed that



$\text{M}(\text{X}\cdots\text{R})$ systems ($\text{X} = \text{halogen}$, $\text{R} = \text{alkyl}$ or aryl) have $\text{M}-\text{X}-\text{R}$ angles in the range $100\text{--}105^\circ$.¹¹ This we interpreted as indicating that the p-type lone pairs of the halocarbon are more basic than the sp lone pair (see diagram 5), leading to an ideal angle near 90° . The observed angles were always $>90^\circ$, which was ascribed to steric hindrance between R and the metal complex. If the Au–X bonding situation (6) is similar to the halocarbon case, ideal $\text{Au}-\text{X}\cdots\text{HN}$ angles of 90° are reasonable.



Analogy with Hydrogen Halide Complexes. In 1984, after we found that halocarbon complexes of the type $[\text{L}_n\text{M}(\text{XR})]$ were stable,¹¹ we tried to synthesize hydrogen halide complexes, always without success, because protonation of an $[\text{L}_n\text{M}-\text{X}]$ system always led either to protonation at the metal to give $[\text{L}_n\text{M}(\text{H})\text{X}]^+$ or protonation of X with dissociation of HX. The hydrogen-bonded system described in this paper is related to an HX complex in the sense that the $\text{H}\cdots\text{X}$ interaction is weak but not absent.

(10) Allinger, N. L. *Adv. Phys. Org. Chem.* 1976, 13, 2.

(11) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* 1990, 99, 89.

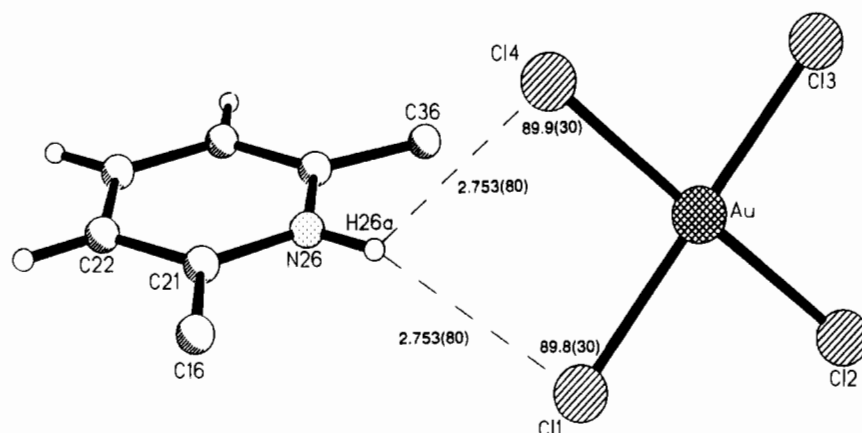


Figure 2. Details of the 3-center H-bond (phenyl rings omitted). The distances shown refer to the normalized H atom position.

Table 1. Summary of Crystallographic Data for the Title Complex

chem formula	C ₁₇ H ₁₄ AuCl ₄ N	fw	571.1
<i>a</i>	9.380(2) Å	space group	<i>P</i> 1
<i>b</i>	10.219(3) Å	<i>T</i>	18 °C
<i>c</i>	11.678(4) Å	λ	0.710 73 Å
α	89.33(2)°	ρ (calc)	2.039 g/mL
β	68.85(2)°	μ	84.81 cm ⁻¹
γ	64.67(2)°	<i>R</i> (<i>F</i>) ^a	3.92%
<i>V</i>	930.0(5) Å ³	<i>R</i> _w (<i>F</i>) ^a	4.37%
<i>Z</i>	2		

^a Quantity minimized = $\sum w\Delta^2$; $R = \sum \Delta / \sum (F_o)$; $R_w = \sum \Delta w^{1/2} / \sum (F_o w^{1/2})$, $\Delta = |F_o - F_c|$.

Table 2. Selected Distances (Å) and Angles (deg) for **4**

Au-Cl(1)	2.286(3)	H _c (26a)-Cl(1)-Au	89.8(30)
Au-Cl(2)	2.270(4)	H _c (26a)-Cl(4)-Au	89.9(30)
Au-Cl(3)	2.265(3)	Cl(1)-Au-Cl(2)	90.3(1)
Au-Cl(4)	2.281(3)	Cl(2)-Au-Cl(3)	89.8(1)
N(26)-H _c (26a)	0.9	Cl(3)-Au-Cl(4)	89.6(1)
N(26)-H _c (26a)	1.03 ^a	Cl(4)-Au-Cl(1)	90.3(1)
H _c (26a)-Cl(1)	2.753(80)	Cl(4)-Au-Cl(2)	179.3(1)
H _c (26a)-Cl(4)	2.753(80)	Cl(3)-Au-Cl(1)	179.0(1)

^a Normalized distance (see text).

Conclusion

The title salt contains an unexpected three-center hydrogen bond. The data suggest that M-X···HN hydrogen bonding is significant and that an M-X···H angle of 90° is favorable for the interaction, probably because of the higher basicity of the p-type Cl lone pair relative to the sp-lone pair. 2,6-Diphenylpyridinium ion, with its high steric bulk, may be a particularly useful cation for giving H-bonded species. Further examples are needed to help eliminate the possibility that special effects, such as packing forces, are operating in this system.

Experimental Section

¹H NMR spectra was recorded on an Omega 300 instrument. Chemical shifts were measured with reference to the residual solvent resonances. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer, using Nujol mulls between NaCl windows. Reagents were purchased from Aldrich Chemical Co.

2,6-Diphenylpyridinium Tetrachloroaurate (3). KAuCl₄ (755 mg, 2 mmol) was dissolved in THF (5 mL), and the solution was treated with 2,6-diphenylpyridine (462 mg, 2 mmol). The acidic (pH = 2) solution was evaporated to give yellow microcrystals which were recrystallized from THF/toluene to give yellow prisms (650 mg, 57%). The characterization was carried out by crystallography. IR (cm⁻¹): 3278 s, 3200 s, 3143 m, 2975 w, 1623 s. ¹HNMR in CD₃CN (δ (ppm), multiplicity, integration): 14.5 br, 1H; 8.78, dd, 1H; 8.40, d, 2H; 8.0, m, 4H; 7.75, m, 6H.

Crystallographic Studies. Crystal, data collection, and refinement parameters are given in Table 1. A suitable crystal was selected and

Table 3. Atomic Coordinates for ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å² $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Au	458.2(5)	2335.7(4)	2399.8(3)	35(1)
Cl(1)	1669(4)	3339(3)	807(3)	69(2)
Cl(2)	147(5)	4048(3)	3812(3)	73(2)
Cl(3)	-697(4)	1313(3)	3974(2)	63(2)
Cl(4)	741(4)	614(3)	997(2)	59(2)
C(11)	3330(18)	1011(8)	-2106(5)	56(6)
C(12)	5101	491	-2529	71(7)
C(13)	5999	756	-3675	65(6)
C(14)	5126	1540	-4397	60(6)
C(15)	3355	2060	-3974	48(5)
C(16)	2456	1795	-2829	41(5)
C(21)	590(12)	2316(9)	-2413(8)	35(4)
C(22)	-161(13)	2375(11)	-3238(9)	45(5)
C(23)	-1914(14)	2792(10)	-2781(10)	53(6)
C(24)	-2887(13)	3141(11)	-1505(10)	52(5)
C(25)	-2109(12)	3090(9)	-710(8)	37(4)
N(26)	-399(9)	2678(8)	-1183(7)	35(4)
C(31)	-4252(8)	2964(7)	1242(6)	63(6)
C(32)	-5182	3343	2528	74(7)
C(33)	-4897	4221	3239	68(6)
C(34)	-3682	4719	2663	56(6)
C(35)	-2752	4340	1376	45(5)
C(36)	-3037	3463	666	37(4)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

mounted with epoxy cement to a glass fiber. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 25 reflections ($20^\circ \leq 2\theta \leq 25^\circ$).

No evidence of a symmetry higher than triclinic was observed in either the photographic or the diffraction data. *E*-statistics suggested a centrosymmetric space group and *P*1 was chosen and subsequently verified by the chemically reasonable results of the refinement. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis, and refined by a full-matrix least-squares procedure. Phenyl rings were refined as rigid bodies with idealized geometry. All non-hydrogen atoms were refined with anisotropic displacement coefficients. An ellipsoid absorption correction was applied to the data set. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We thank the NSF for support.

Supplementary Material Available: Tables listing structure determination details, bond lengths and angles, anisotropic displacement parameters, and H-atom coordinates and *U* values (5 pages). Ordering information is given on any current masthead page.