Bis(acetato)bis[4-(*N*-acetylamino)pyridine]aquacopper(II)–Hydrogen Fluoride–Hydrate (1/2/2): *X*-Ray Structure reveals H_2O·HF Hydrogen Bonded in the Lattice†

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The elusive adduct H_2O·HF has been discovered in crystals of a copper(II) acetate–aminopyridine complex. The hydrogen-bond length $R(O \cdots F)$ is 2.749 Å.

The hydrogen-bonded dimer H_2O·HF has been studied in the gas phase by microwave[1–4] and i.r.[5] spectroscopy and information about its structure and energy obtained. *Ab initio* calculations had predicted that the dimer will be $H_2O \cdots HF$ rather than $HOH \cdots FH$ or any of the bifurcated conformations.[6,7] Predictions about hydrogen-bond lengths and energy have also been made: $R(O \cdots F) = 2.60$ Å, $\Delta E = 32$ kJ mol^{-1};[8] 2.47 Å, 27 kJ mol^{-1};[9] 2.91 Å, 23 kJ mol^{-1};[10] and 2.680 Å, 37 kJ mol^{-1}.[11] A recent bond-energy calculation indicates a strong bond of 66 kJ mol^{-1},[12] although a measured value of 26 kJ mol^{-1} had previously been obtained from i.r. data.[5] Microwave studies of H_2O·HF have however been most fruitful and yielded information about the complex's conformation,[13] H–F bond changes,[3] electric dipole moment,[2] and potential-energy constants.[4]

In the liquid phase, hydrofluoric acid has always been an anomaly[14] because of its unexpectedly high pK_a of 3.18.[15] The explanation, that this indicates undissociated HF(aq), has been challenged, and an alternative theory advanced involving a strongly hydrogen-bonded species $H_2\overset{+}{O}–H \cdots \overset{-}{F}$.[16–18] Cyclic bifurcated structures in aqueous solution have also been proposed.[19] In 1981 the *X*-ray crystal structures of solid-phase H_2O·HF and H_2O·2HF were published.[20] The shortest $R(O \cdots F)$ in these adducts was 2.464 and 2.453 Å respectively. The crystals were in effect $H_3O^+F^-$ and $H_3O^+HF_2^-$, although in the latter case the proton of the difluoride ion was asymmetrically placed and $R(F \cdots F)$ was 2.367 Å as opposed to the more normal 2.26 Å for this ion in KHF_2.[21] It comes as something of a surprise to find in the crystals of the compound $[Cu\{NC_5H_4(NHCOCH_3)\text{-}4\}_2(CH_3CO_2)_2(H_2O)]\cdot 2HF\cdot 2H_2O$ that H_2O·HF is present in the lattice and that the $R(O \cdots F)$ distance suggests that proton transfer between them has not occurred.

Experimental

Synthesis of 4-(N-*Acetylamino*)*pyridinium Acetate*.—4-Aminopyridine (5 g, 53 mmol) was refluxed with acetic anhydride (5.2 cm^3, 53 mmol) for 2 h. On cooling, the product solidified and was recrystallized from diethyl ether to give colourless crystals of 4-(*N*-acetylamino)pyridinium acetate, m.p. 93 °C (Found: C, 55.10; H, 6.10; N, 14.30. Calc. for $C_9H_{12}N_2O_3$: C, 55.10; H, 6.15; N, 14.30%).

Synthesis of Bis(*acetato*)*bis*[4-(N-*acetylamino*)*pyridine*]*aquacopper*(II)*–Hydrogen Fluoride–Hydrate* (1/2/2).—4-(*N*-Acetylamino)pyridinium acetate (1.96 g, 10 mmol) was dissolved in water (50 cm^3) to which CuF_2 (0.5 g, 5 mmol) was added and the solution stirred. After 30 min a clear blue solution was obtained, which was reduced to a third of its volume on a rotary evaporator and left to stand. Within 1 day, small, royal blue crystals formed and were recrystallized from a minimum volume of water slowly to give crystals of $[Cu\{NC_5H_4(NHCOCH_3)\text{-}4\}_2(CH_3CO_2)_2(H_2O)]\cdot 2HF\cdot 2H_2O$, m.p. 235 °C (decomp.) (Found: C, 39.60; H, 5.70; F, 7.20; N, 10.25. $C_{18}H_{30}CuF_2N_4O_9$ requires C, 39.45; H, 5.50; F, 6.95; N, 10.25%.) The i.r. spectrum, run on a Perkin-Elmer 983G spectrometer, as a KBr disc, showed absorbances at 3 251, 3 086, 3 050, 3 010, 2 921, and 2 853 cm^{-1} superimposed on a very broad and intense band centred at *ca.* 3 350 cm^{-1}. Other peaks were at 1 709vs, 1 689vs, 1 594vs, vbr, 1 513vs, 1 426vs, 1 400vs, 1 369vs, 1 326vs, 1 306vs, 1 242vs, 1 205vs, 1 108w, 1 063s, 1 026vs, 1 007s, 932w, 843vs, 780s, 735m, 676vs, 624s, 552vs, 539vs, 371w, 344m, and 272m cm^{-1}. Broad bands also underlay the spectrum centred at *ca.* 1 500 and 700 cm^{-1}.

Crystallographic Studies.—Crystal data were collected on an Enraf-Nonius CAD-4 diffractometer using a ω—2θ scan procedure.[22]

Crystal data. $C_{18}H_{30}CuF_2N_4O_9$, $M = 547.999$, $a = 15.127(2)$, $b = 6.746(2)$, $c = 24.483(3)$ Å, $\beta = 96.06(1)°$, space group $C2/c$, $U = 2\,484.36$ Å^3, $Z = 4$, $D_c = 1.465$ g cm^{-3}, $F(000) = 1\,140$, $\mu(\text{Cu-}K_\alpha) = 18.2$ cm^{-1}, $\lambda = 1.5418$ Å, 20 °C, crystal dimensions 0.75 × 0.25 × 0.23 mm.

Data collection, solution, and refinement. The intensities of 2 359 unique reflections ($\theta_{max.} = 70°$) were measured, of which 2 114 satisfied the criterion $I > 3.0\sigma(I)$ and were used in the refinement. The segment of reciprocal space scanned was h −18 to 18, k 0 to 8, l 0 to 29. The reflection intensities were corrected for aborption, using the azimuthal-scan method;[23] maximum transmission factor 1.00, minimum value 0.94.

The structure was solved *via* the heavy-atom method, Cu–O(1) being on a crystallographic two-fold axis. Refinement proceeded by standard full-matrix least squares.[24] Towards the end of the refinement two lattice peaks, of approximately equal intensity, were located from a Fourier difference map. Two factors persuaded us that both these sites are occupied by a mixture of HF and H_2O molecules: (*i*) elemental analysis figures; and (*ii*) a chemically feasible hydrogen-bonding network was maintained throughout the whole lattice. We concluded that, although the exact ratio of HF to H_2O cannot be unequivocally ascertained, the most appropriate model to adopt is that of an equal mixture of both HF and H_2O for each of the two positions. Scattering factor coefficients for an equal mixture of O and F were calculated.[25]

All non-hydrogen atoms, except the disordered O/F mixtures, were refined anisotropically, and hydrogen atoms of the acetylaminopyridine and acetate ligands were placed in calculated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $[Cu\{NC_5H_4(NHCOCH_3)\text{-}4\}_2(CH_3CO_2)_2(H_2O)]\cdot 2HF\cdot 2H_2O$

Atom	*x*	*y*	*z*
Cu	0	2 834(1)	2 500
O(1)	0	−758(7)	2 500
O(2)	1 259(2)	2 791(5)	2 790(1)
O(3)	1 220(2)	6 065(5)	2 841(1)
O(4)	−1 288(3)	7 381(6)	4 881(2)
N(1)	−348(2)	3 158(6)	3 266(1)
N(2)	−1 136(3)	4 049(6)	4 841(2)
C(1)	1 631(3)	4 477(7)	2 889(2)
C(2)	2 613(3)	4 445(9)	3 064(2)
C(3)	−376(3)	1 684(7)	3 630(2)
C(4)	−634(3)	1 956(7)	4 153(2)
C(5)	−871(3)	3 840(7)	4 316(2)
C(6)	−831(4)	5 356(8)	3 945(2)
C(7)	−576(4)	4 943(8)	3 433(2)
C(8)	−1 350(4)	5 754(8)	5 084(2)
C(9)	−1 685(4)	5 487(8)	5 641(2)
OF(1)*	1 818(3)	9 452(6)	3 459(2)
OF(2)*	−3 582(4)	4 282(7)	4 528(2)

* $OF = \frac{1}{2}O + \frac{1}{2}F$.

Table 2. Bond lengths (Å) and angles (°)

O(1)–Cu	2.423(7)	O(2)–Cu	1.961(5)
N(1)–Cu	2.012(5)	C(1)–O(2)	1.281(6)
C(1)–O(3)	1.238(7)	C(8)–O(4)	1.213(7)
C(3)–N(1)	1.340(7)	C(7)–N(1)	1.328(7)
C(5)–N(2)	1.393(6)	C(8)–N(2)	1.351(7)
C(2)–C(1)	1.502(8)	C(4)–C(3)	1.389(7)
C(5)–C(4)	1.390(7)	C(6)–C(5)	1.373(7)
C(7)–C(6)	1.379(7)	C(9)–C(8)	1.514(8)
O(2)–Cu–O(1)	89.2(2)	N(1)–Cu–O(1)	96.2(2)
N(1)–Cu–O(2)	90.3(2)	O(2′)–Cu–O(2)	178.3(2)
N(1′)–Cu–N(1)	167.5(2)	O(2′)–Cu–N(1)	89.9(2)
C(1)–O(2)–Cu	116.5(4)	C(3)–N(1)–Cu	124.7(4)
C(7)–N(1)–Cu	119.2(4)	C(7)–N(1)–C(3)	116.1(5)
C(8)–N(2)–C(5)	126.8(5)	O(3)–C(1)–O(2)	122.9(5)
C(2)–C(1)–O(2)	116.3(5)	C(2)–C(1)–O(3)	120.8(6)
C(4)–C(3)–N(1)	123.2(5)	C(5)–C(4)–C(3)	119.4(5)
C(4)–C(5)–N(2)	117.7(5)	C(6)–C(5)–N(2)	124.9(5)
C(6)–C(5)–C(4)	117.4(5)	C(7)–C(6)–C(5)	119.2(6)
C(6)–C(7)–N(1)	124.7(5)	N(2)–C(8)–O(4)	123.8(5)
C(9)–C(8)–O(4)	121.7(5)	C(9)–C(8)–N(2)	114.5(5)

Key to symmetry operation relating designated atoms to reference atoms at (*x*, *y*, *z*): (′) −*x*, *y*, 0.5 − *z*.

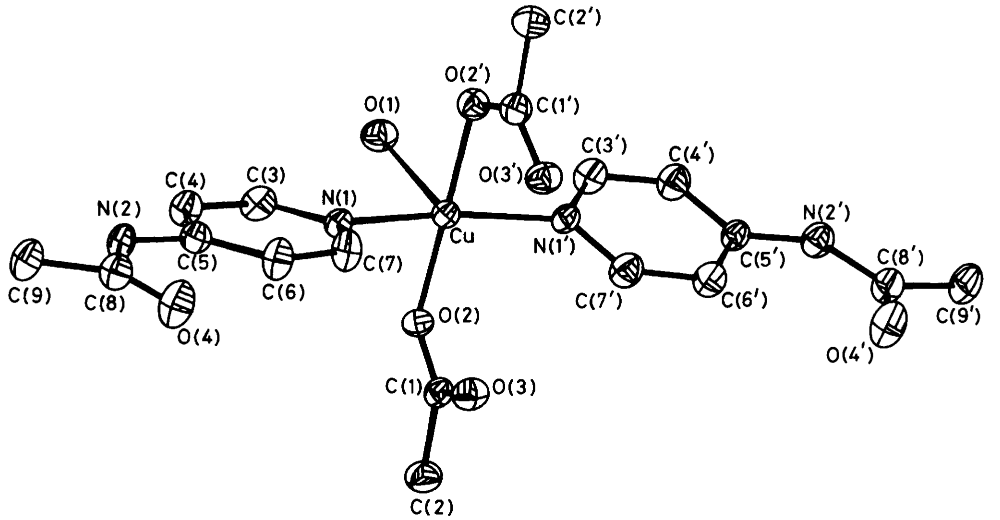

Figure 1. The molecular structure of $[Cu\{NC_5H_4(NHCOCH_3)\text{-}4\}_2(CH_3CO_2)_2(H_2O)]$. Hydrogen atoms have been omitted for clarity. The Cu–O(1) bond lies on a crystallographic two-fold axis; symmetry operation (′) = −*x*, *y*, 0.5−*z*

positions (C–H and N–H 0.96 Å, $U = 0.10$ Å^2). The final residuals *R* and *R′* were 0.069 and 0.073 respectively. The function minimized was $\Sigma_w(|F_o| - |F_c|)^2$ with the weight, *w*, being defined as $1/[\sigma^2(F_o) + 0.000\,01F_o^2]$. A total of 159 variables were refined.

All computations were made on a DEC VAX-11/750 computer. Table 1 lists the atomic co-ordinates, Table 2 the bond lengths and angles. The structure is shown in Figures 1 (the complex) and 2 (the unit cell). Hydrogen-bond data are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Discussion

As part of a study of the hydrogen bonding between ligand fluoride and lattice water, our intention at the start of the work reported here was to prepare a complex of CuF_2 and 4-*N*-(acetylamino)pyridine. A previous pyridine amide complex $[Cu(na)_2F_2(H_2O)_2]\cdot 4H_2O$, na = nicotinamide, had revealed Cu–F ··· H_2O hydrogen bonds that were short[26] and it was in the hope of finding another example that the 4-*N*-(acetylamino)pyridine ligand was chosen. The related 2-*N*-acetylamino ligand is a good chelating ligand for Cu^{II},[27] but since chelation was not desirable, we chose the former. In making the ligand, however, we inadvertently obtained the salt 4-*N*-(acetylamino)-pyridinium acetate which reacted with CuF_2 to form a non-fluoride complex according to equation (1). Clearly under these

$$CuF_2 + 2[^{+}NHC_5H_4(NHCOCH_3)\text{-}4]CH_3CO_2^{-} + 3H_2O \longrightarrow [Cu\{NC_5H_4(NHCOCH_3)\text{-}4\}_2(CH_3CO_2)_2(H_2O)]\cdot 2HF\cdot 2H_2O \quad (1)$$

conditions the acetate is the preferred ligand even though HF is

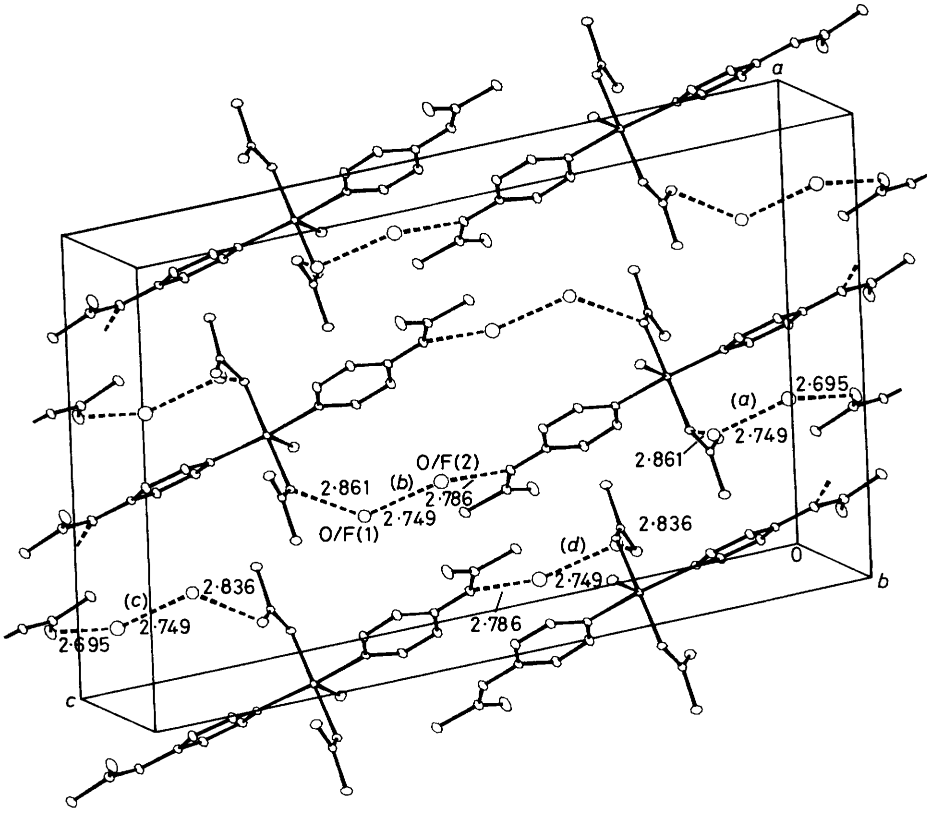

Figure 2. A unit-cell packing diagram showing the hydrogen-bonding network of the lattice H_2O/HF molecules, with hydrogen-bond distances (Å)

Table 3. Hydrogen bond lengths (Å)

O/F*(1) ··· O(3)	2.836	O/F*(2) ··· N(2c)	2.786
O/F*(1) ··· O(2a)	2.861	O/F*(2) ··· O/F*(1d)	2.749
O/F*(2) ··· O(4b)	2.695	O(3) ··· O(1a)	2.893

* O/F = $\frac{1}{2}$O + $\frac{1}{2}$F. Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (a) *x*, 1.0 + *y*, *z*; (b) −0.5 − *x*, 1.5 − *y*, 1.0 − *z*; (c) −0.5 − *x*, 0.5 − *y*, 1.0 − *z*; (d) −0.5 + *x*, −0.5 + *y*, *z*.

the stronger acid [pK_a = 3.18 compared to pK_a (CH_3CO_2H) = 4.76].[15] By a fortuitous set of circumstances, crystals of a neutral complex were obtained in which HF was present as solvate, along with H_2O. The *X*-ray crystal structure revealed that the complex molecules were interlinked *via* hydrogen-bond chains incorporating HF and H_2O probably in a random pattern, Figure 2.

The hydrogen bonding occurs between an acetate oxygen on one complex and an amide nitrogen or oxygen of another. There are four types of hydrogen bond chain (see Figure 2): (*a*) O(2) ··· O/F(1) ··· O/F(2) ··· O(4), (*b*) O(2) ··· O/F(1) ··· O/F(2) ··· N(2), (*c*) O(3) ··· O/F(1) ··· O/F(2) ··· O(4), and (*d*) O(3) ··· O/F(1) ··· O/F(2) ··· N(2). The respective lengths are given in Table 3. The middle 'link' of O/F ··· O/F is 2.749 Å. This is not significantly shorter than the links to the acetate oxygens, 2.861 and 2.836 Å (to the co-ordinating and non-co-ordinating oxygens respectively) or to the amide atoms, 2.695 and 2.786 Å (to the amide oxygen and nitrogen atoms respectively). For this reason we believe that proton transfer from HF to either H_2O or to the amide nitrogen has not occurred. Such transfer would result in much stronger and shorter hydrogen bonds.[28]

Consequently we feel confident in postulating the species $H_2O{\cdot}HF$ as being present in the crystals with an *R*(O ··· F) of the order predicted. One other example of hydrogen bonding between a ligand with an NH group and a fluoride in the lattice is known, $[Cu(Him)_4(H_2O)_2]F_2$ (Him = imidazole).[29] In this case *R*(N ··· F) = 2.65 Å and *R*(O ··· F) = 2.70 Å. As Figure 2 reveals, the amide nitrogens retain their sp^2 character and consequently we take this as an indication that the NH bond is acting as a hydrogen-bond donor. The N ··· O/F distance suggests that this donor bond is between NH and a neutral species, HF or H_2O, rather than an ionic F^- or H_3O^+.

The i.r. evidence supports our assertion that the hydrogen bonding in the crystal is not very strong. There are three broad and intense bands underlying the spectrum and centred at *ca.* 3 350, 1 500, and 700 cm^{-1}. Had there been a short hydrogen bond it would have led to an i.r. absorption at *ca.* 2 000 cm^{-1}.[30] The band at 3 350 cm^{-1} is in the region of that at 3 500 cm^{-1} reported by Thomas[5] for gas-phase $H_2O{\cdot}HF$, and the band at 700 cm^{-1} likewise has its counterpart at 676 and 624 cm^{-1} for the in- and out-of-phase bending modes of gas-phase $H_2O{\cdot}HF$. Lister and Palmieri's alternative assignments[31] do not materially alter our belief that the hydrogen-bonding modes would be in the 3 350 and 700 cm^{-1} region. The hydrogen-bond bending modes are at 1 500 (in-plane) and 700 cm^{-1} (out-of-plane) for the interlinking hydrogen bonds.

The complex itself consists of a square-planar arrangement of two acetate oxygens and two pyridine-ring nitrogens co-ordinated to a copper atom 0.07 Å above the basal plane. A water molecule occupies the apex with *R*(Cu–O) = 2.423(7) Å typical of a ligand water in such a configuration. Bands in the i.r. allocatable to the ligand bonds are 780 [ν(Cu–O)], 552 [ν(Cu–

N)], 344 [δ(Cu–O)], and 272 [δ(Cu–N)] cm^{-1}. These have their counterparts in the spectrum of $[Cu(na)_2F_2(H_2O)_2]\cdot 4H_2O$ [26] and of other complexes.[30,32,33]

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