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Crystal Structure of a Polymeric 2:1 Complex of Nicotinic Acid with Copper(I) Chloride

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While isonicotinic acid (HINA) forms only 1:1 adducts with copper(I) halides [1], nicotinic acid (HNA) yields complexes of both 1:1 and 2:1 HNA/CuX molar ratios [2]. Recently we reported the crystal structure of (HINA)CuCl, which comprises $(Cu_2Cl_2)_\infty$ polymeric stairs cross-linked by virtually planar hydrogen-bonded $(HINA)_2$ dimers, with each ring nitrogen atom coordinating to a metal center [3]. We have now succeeded in preparing good crystals of the title $(HNA)_2CuCl$ complex, and accordingly carried out an X-ray analysis to determine its mode of coordination and possible polymerization.

Experimental

Preparation of the $(HNA)_2CuCl$ Complex

Nicotinic acid (1.45 g, 12 mmol) dissolved in boiled ethanol (50 ml) was filtered and then added to an ethanolic solution of $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol; 40 ml) followed by addition of excess L-(+)-ascorbic acid (vitamin C). The mixture was boiled until a clear orange–red solution was obtained. Upon cooling of this final mixture in a stoppered conical flask, the complex separated as bright red needles which were filtered off at the pump, washed with ethanol, and dried under vacuum. *Anal.* Found for formula $C_{12}H_{10}N_2ClCuO_4$ (calculated values in parentheses): C, 41.23(41.75); H, 3.00(2.92); N, 8.00(8.11); Cu, 18.50(18.41)%.

X-ray Structure Determination

A single crystal of dimensions *ca.* 0.24 × 0.20 × 0.14 mm was centered on a Nicolet R3m four-circle diffractometer. Unit-cell determination and intensity data collection and processing followed established procedures in our laboratory [4], and pertinent information is summarized in Table I.

Structure solution was achieved by Patterson and Fourier methods. All twenty non-hydrogen atoms in the asymmetric unit were refined anisotropically. The

TABLE I. Data Collection and Processing Parameters for $(HNA)_2CuCl$

Molecular formula	$C_{12}H_{10}N_2ClCuO_4$
Molecular weight	345.21
Cell constants	a = 3.7752(5), b = 6.301(1), c = 26.754(8) Å, β = 90.96(2)°, V = 636.3(2) Å^3, Z = 2
Density (flotation in CCl_4/CH_2I_2)	1.810 g cm^{-3}
Density (calc.)	1.802 g cm^{-3}
Space group	*Pc* (No. 7)
Radiation	graphite-monochromatized Mo Kα, λ = 0.71069 Å
Absorption coefficient	18.98 cm^{-1}
Mean μr	0.18
Transmission factors	0.547 to 0.662
Scan type and speed	ω–2θ; 2.02–8.37 deg min^{-1}
Scan range	1° below Kα_1 to 1° above Kα_2
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	$h, k, \pm l, 2\theta_{\max} = 52°$
Unique data measured	1385
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	1225
Number of variables, p	179
$R_F = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.034
Weighting scheme	$w = [\sigma^2(F_o) + 0.0005\lvert F_o\rvert^2]^{-1}$
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.043
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.451
Residual extrema in final difference map	0.49 to −0.34 e Å^{-3}

0020-1693/87/$3.50

TABLE II. Atomic Coordinates ($\times 10^3$ for x, $\times 10^4$ for y and z) and Equivalent Isotropic Temperature Factors[a]

Atom	x	y	z	U_{eq}
Cu	0	1204(1)	0	42(1)
Cl	–495(1)	–1088(1)	10(2)	39(1)
N(1)	–29(2)	2780(13)	655(3)	26(2)
O(1)	–419(2)	–298(10)	1880(3)	55(3)
O(2)	–297(3)	2442(12)	2371(3)	54(3)
C(1)	–155(3)	1893(15)	1063(4)	34(3)
C(2)	–165(3)	2820(18)	1523(4)	38(3)
C(3)	–38(1)	4755(7)	1600(2)	29(1)
C(4)	104(3)	5872(16)	1190(4)	35(3)
C(5)	93(2)	4837(15)	709(4)	28(3)
C(6)	–309(1)	1417(9)	1954(2)	33(2)
N(2)	42(3)	2911(15)	–646(3)	37(3)
O(3)	296(3)	2326(11)	–2390(3)	58(3)
O(4)	453(2)	–298(12)	–1864(3)	45(2)
C(7)	175(3)	1799(15)	–1043(3)	28(3)
C(8)	166(2)	2689(15)	–1527(4)	22(2)
C(9)	26(2)	4850(7)	–1571(2)	43(2)
C(10)	–80(3)	5828(15)	–1158(4)	41(3)
C(11)	–87(3)	4819(18)	–727(4)	41(4)
C(12)	307(2)	1626(7)	–1940(2)	36(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U matrix.

eight ring H atoms were geometrically generated (C–H fixed at 0.96 Å), assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent C atoms in the final least-square cycles, which converged to the R_F and R_w indices given in Table I. The carboxylic H atoms could not be located in the final difference map.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package [5]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [6].

The final atomic parameters are listed in Table II; atom labelling follows that shown in Fig. 1. Bond distances and angles are tabulated in Table III. See also 'Supplementary Material'.

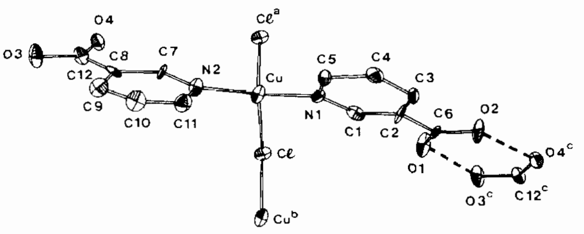

Fig. 1. Atom labelling and principal structural features of polymeric $(HNA)_2CuCl$, with hydrogen bonds represented by broken lines. The thermal ellipsoids are drawn at the 30% probability level, and symmetry transformations are as given in Table III.

Discussion

The structure determination of $(HNA)_2CuCl$ confirms the presence of carboxylic acid dimers as inferred by infrared spectroscopy [1]. The asymmetric unit (Fig. 1) corresponds exactly to the 2:1 nicotinic acid–copper(I) chloride stoichiometry. The Cu and Cl atoms are arranged alternately to form a polymeric zigzag chain [$Cl–Cu–Cl^a = 105.2(2)°$, $Cu–Cl–Cu^b = 105.2(4)°$] extending along the very short a axis. The nearly planar, hydrogen-bonded nicotinic acid dimer [torsion angles $C(6)–O(1)\cdots O(3)^c–O(12)^c = –8(2)°$, $C(6)–O(2)\cdots O(4)^c–C(12)^c = –4(2)°$] is 'diagonally' linked, via their nitrogen lone pairs, to two metal centers belonging to adjacent $(CuCl)_\infty$ chains and separated by the $(-\boldsymbol{a} + \boldsymbol{c})$ vector (Fig. 2). The coordination geometry about the copper(I) atom is thus approximately tetrahedral (Table III), and the resulting crystal structure comprises layers parallel to the (010) set of planes.

In many aspects the polymeric structure of $(HNA)_2CuCl$ is similar to that of the previously reported (HINA)CuCl complex [3], the present $(CuCl)_\infty$ chain taking the place of the $(Cu_2Cl_2)_\infty$ stair (or ribbon) in the latter. While the measured Cu–N bond distances (Table III) lie within the range of 2.00–2.05 Å for copper(I) complexes with pyridine and substituted pyridine ligands [7], the Cu–Cl bonds (Table III) are much shorter than those expected (2.24–2.40 Å) for terminal $Cu^I–Cl$ bonds [8], as well as the values 2.434(2)–2.470(2) Å found in dimeric $[(2\text{-Mepy})_2CuCl]_2$ [9].

Complexes of stoichiometry L_2CuX, where L = pyridine or substituted pyridine and X = halogen, commonly exist as bis(μ-halo)-bridged $(L_2CuX)_2$ dimers with a cyclic Cu_2X_2 core [9–11]. Rarer examples of the mononuclear, pseudo trigonal planar L_2CuX complex are found in two crystalline phases of $(2,6\text{-Me}_2py)_2CuI$ [10], and in $(2,6\text{-Me}_2py)_2CuCl$ and $(2,6\text{-Me}_2py)_2CuBr$ [12], in which steric crowding of the methyl substituents helps to prevent dimerization of the monomeric units in solution. To our knowledge the title compound constitutes the first example of a polymeric structure of L_2CuX stoichiometry, the existence of which may be ascribed to the stabilizing influence of the hydrogen-bonded nicotinic acid dimer.

Supplementary Material

Tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors are available from the Editor-in-Chief.

TABLE III. Bond Lengths (Å) and Bond Angles (°)

Cu–Cl	2.363(4)	Cu–Cl^{a}	2.391(4)
Cu–N(1)	2.020(8)	Cu–N(2)	2.044(9)
N(1)–C(1)	1.323(13)	N(1)–C(5)	1.382(13)
O(1)–C(6)	1.173(9)	O(2)–C(6)	1.289(8)
C(1)–C(2)	1.362(14)	C(2)–C(3)	1.325(12)
C(2)–C(6)	1.560(11)	C(3)–C(4)	1.417(11)
C(4)–C(5)	1.443(14)	N(2)–C(7)	1.375(13)
N(2)–C(11)	1.314(15)	O(3)–C(12)	1.280(9)
O(4)–C(12)	1.347(9)	C(7)–C(8)	1.412(12)
C(8)–C(9)	1.465(11)	C(8)–C(12)	1.405(11)
C(9)–C(10)	1.333(12)	C(10)–C(11)	1.316(15)
O(1)···O(3)^{c}	2.58(2)	O(2)···O(4)^{c}	2.64(2)
Cl–Cu–Cl^{a}	105.2(2)	Cl–Cu–N(1)	103.7(3)
Cl–Cu–N(2)	113.8(3)	Cl^{a}–Cu–N(1)	110.0(3)
Cl^{a}–Cu–N(2)	104.7(3)	N(1)–Cu–N(2)	118.8(4)
Cu–Cl–Cu^{b}	105.2(4)	Cu–N(1)–C(1)	122.3(7)
Cu–N(1)–C(5)	121.9(7)	C(1)–N(1)–C(5)	115.7(8)
N(1)–C(1)–C(2)	125.4(10)	C(1)–C(2)–C(3)	121.4(9)
C(1)–C(2)–C(6)	116.1(9)	C(3)–C(2)–C(6)	122.4(7)
C(2)–C(3)–C(4)	118.5(7)	C(3)–C(4)–C(5)	117.4(8)
N(1)–C(5)–C(4)	121.4(9)	O(1)–C(6)–O(2)	128.0(6)
O(1)–C(6)–C(2)	121.6(6)	O(2)–C(6)–C(2)	110.4(6)
Cu–N(2)–C(7)	114.8(7)	Cu–N(2)–C(11)	126.0(8)
C(7)–N(2)–C(11)	118.5(9)	N(2)–C(7)–C(8)	120.2(9)
C(7)–C(8)–C(9)	116.4(8)	C(7)–C(8)–C(12)	121.9(8)
C(9)–C(8)–C(12)	121.5(7)	C(8)–C(9)–C(10)	118.5(7)
C(9)–C(10)–C(11)	120.8(9)	N(2)–C(11)–C(10)	125.1(11)
O(3)–C(12)–O(4)	117.3(6)	O(3)–C(12)–C(8)	124.6(6)
O(4)–C(12)–C(8)	118.0(6)	C(6)–O(1)···O(3)^{c}	119(2)
C(6)–O(2)···O(4)^{c}	114(2)	O(1)···O(3)^{c}–C(12)^{c}	122(2)
O(2)···O(4)^{c}–C(12)^{c}	120(2)		

Symmetry transformation: $^{a}1 + x, y, z$; $^{b}-1 + x, y, z$; $^{c}-1 + x, -y, 1/2 + z$.

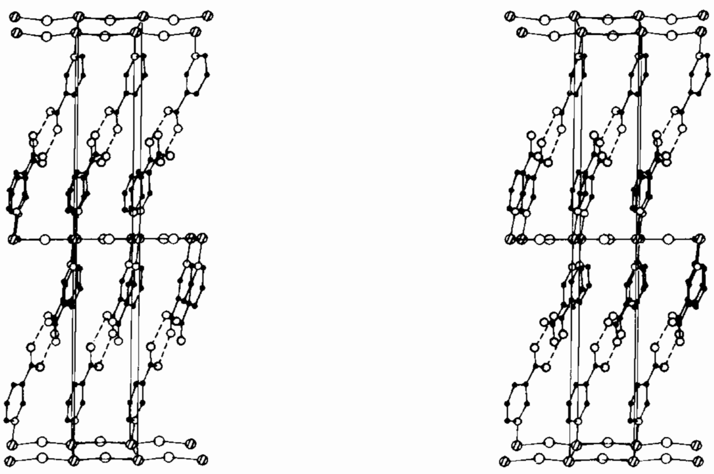

Fig. 2. Stereodrawing of the crystal structure of $(HNA)_2CuCl$. The unit-cell origin lies at the upper left corner, with *b* pointing towards the reader, *a* from left to right, and *c* downwards.

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