Inorganica Chimica Acta, 101 (1985) L27–L30

Crystal Structure of a Polymeric 1:1 Complex of Copper(I) Chloride with Isonicotinic Acid*

MOHAMED A. S. GOHER

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

and THOMAS C. W. MAK

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received February 18, 1985

Previous work has established that isonicotinic acid (HINA) forms only 1:1 adducts with copper(I) halides, whereas ethyl isonicotinate yields complexes with 1:1, 2:1 and 3:1 L/CuX molar ratios [1]. The presence of dimeric hydrogen bonding between two carboxylic acid groups in Cu(HINA)X, as suggested by the infrared data, plausibly accounts for the different behavior of the two γ-substituted pyridines.

Complexes of stoichiometry CuLX are known to exist in varying degrees of oligomerization and many structural configurations, depending principally on the nature of the ligand L [2–4]. Systems which have been studied hitherto involve pnicogen-base ligands such as substituted phosphines, arsines and pyridines which are incapable of donor-hydrogen bond-formation. The mode of polymerization in crystalline Cu(HINA)Cl is therefore of interest, and we have thus carried out an X-ray structure determination.

Experimental

Preparation of the Cu(HINA)Cl Complex

Isonicotinic acid (1.50 g; 10 mmol) dissolved in boiling ethanol (40 ml) was filtered and added to an ethanolic solution of $CuCl_2 \cdot 2H_2O$ (1.70 g; 10 mmol), followed by addition of excess L-(+)ascorbic acid (vitamin C). The mixture was boiled until a clear orange solution was obtained. Upon cooling of this final mixture in a stoppered conical flask, the complex separated as red needles which were filtered off at the pump, washed with ethanol, and dried under vacuum. Elemental analysis (% with calculated values in parentheses for formula $C_6H_5NO_2ClCu$): C 32.60 (32.44); H 2.37 (2.27); N 6.35 (6.30); Cl 15.65 (15.95); Cu 28.70 (28.60). A bromo complex was prepared in the same manner and shown to be isomorphous with the chloro complex by a comparison of their X-ray powder diffraction patterns.

X-Ray Structure Determination

A single crystal of dimensions *ca.* 0.28 × 0.12 × 0.04 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 [5], and pertinent information are summarized in Table I.

TABLE I. Data Collection and Processing Parameters for Cu(HINA)Cl.

Molecular formula	$C_6H_5NO_2ClCu$
Molecular weight	223.90
Cell constants	$a = 14.097(8), b = 3.747(1), c = 14.251(7)$ Å, $\beta = 101.34(4)°, V = 738.1(5)$ Å^3, $Z = 4$
Density (Calcd.)	2.015 g cm^{-3}
Space Group	$P2_1/c$
Radiation	graphite-monochromatized MoKα, λ = 0.71069 Å
Absorption coefficient	32.72 cm^{-1}
Mean μr	0.22
Transmission factors	0.529–0.667
Scan type and speed	$\omega-2\theta$; 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	$h, k, \pm l$; $2\theta_{max} = 46°$
Unique data measured	990
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert), n$	652
Number of variables, p	100
$R_F = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.060
Weighting scheme	$w = [\sigma^2(F_o) + 0.0015\lvert F_o\rvert^2]^{-1}$
$R_{wF} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.068
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.229
Residual extrema	0.62 to −0.67 eÅ^{-3}

---

*Metal Pseudohalide Complexes, Part X. Part IX is ref. 16.

0020-1693/85/$3.30

TABLE II. Atomic Coordinates ($\times 10^4$) and Thermal Parameters^a ($Å^2 \times 10^3$) for Cu(HINA)Cl.

Atom	x	y	z	U_{11}/U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	796(1)	2431(5)	210(1)	62(1)	56(1)	38(1)	2(1)	2(1)	5(1)
Cl	752(2)	7304(7)	−797(2)	55(1)	27(1)	39(1)	3(2)	21(1)	2(2)
N	1808(5)	1799(22)	1391(5)	46(5)	34(6)	32(5)	5(4)	12(4)	−4(4)
C(1)	1675(6)	2777(32)	2265(7)	36(5)	43(7)	41(6)	8(7)	12(5)	8(7)
C(2)	2367(6)	2451(31)	3080(6)	39(5)	29(5)	32(5)	4(6)	12(4)	−9(6)
C(3)	3243(7)	1055(27)	3012(6)	44(6)	29(6)	23(5)	3(5)	11(4)	−5(5)
C(4)	3411(7)	−25(29)	2119(7)	37(6)	31(6)	41(6)	11(5)	5(5)	7(5)
C(5)	2680(7)	396(30)	1354(7)	45(6)	42(7)	32(6)	−14(6)	18(5)	−6(6)
C(6)	4023(7)	637(31)	3878(7)	37(6)	31(7)	44(7)	1(6)	17(5)	5(6)
O(1)	4818(5)	−831(24)	3796(5)	49(4)	80(6)	39(4)	−1(4)	8(3)	14(5)
O(2)	3846(5)	1704(24)	4668(5)	59(4)	87(7)	36(4)	−17(5)	11(3)	22(5)
H(1)	1059	3755	2319	50					
H(2)	2239	3195	3688	50					
H(4)	4020	−1026	2051	50					
H(5)	2791	−360	741	50					

^{a}The anisotropic and isotropic temperature factor exponents take the forms: $-2\pi^2\Sigma\Sigma U_{ij}h_ih_ja_i^* \times a_j^*$ and $-8\pi^2U \sin^2\theta/\lambda^2$, respectively.

Structure solution was achieved by Patterson and Fourier methods. All eleven non-hydrogen atoms in the asymmetric unit were refined anisotropically. The four aromatic 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_G indices given in Table I.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package [6]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [7].

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. A table of structure factors has been deposited with the Editor-in-Chief.

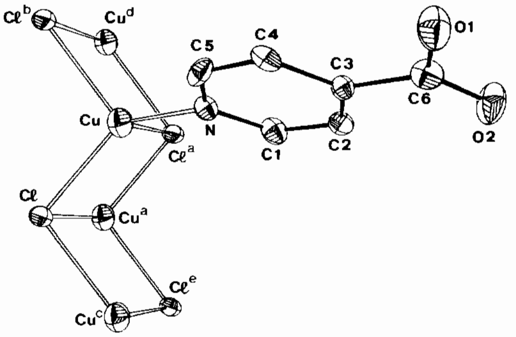

Fig. 1. Atom labelling and principal structural features of polymeric Cu(HINA)Cl. The thermal ellipsoids are drawn at the 30% probability level, and covalent bonds are differentiated from metal–ligand bonds by shading. Symmetry transformations are as indicated in Table III.

Discussion

The structure determination of Cu(HINA)Cl confirms the presence of carboxylic acid dimers as inferred by infrared spectroscopy [1], and also a 'ribbon' or 'stair-polymer' [4] chain of edge-sharing Cu_2Cl_2 parallelograms propagating in the direction of the short b axis (Figs. 1 and 2). Precedents of polymeric structures of this type are complexes of nitrogen bases with copper(I) and silver(I) halides; known examples include Cu(py)Cl [8] and Cu(py)I [9], adducts of CuX (X = Cl, Br, I) with acetonitrile [10, 11], benzonitrile [12], azomethane [13] and 3-methylrhodamine [14], and adducts of AgI with 2- and 3-methylpyridine and quinoline [15].

The asymmetric unit corresponds exactly to the 1:1 copper(I) chloride–isonicotinic acid stoichiometry. The Cu_2Cl_2 rings occupy Wyckoff position 2(a) (0,0,0; 0,½,½), and the polymeric chain is generated by a repetition of lattice translations along b. As a consequence of this, each Cu_2Cl_2 unit in the chain is planar and centrosymmetric, but differs in geometry from its neighboring units. Folding of the stair polymer may be described by the dihedral angle between two successive Cu_2Cl_2 units, which has the value 67.7°.

The hydrogen-bonded, virtually planar isonicotinic acid dimers are centered at Wyckoff position 2(d) (½,0,½; ½,½,0), and each are 'diagonally' linked, via their nitrogen lone pairs, to two metal centers in $(Cu_2Cl_2)_\infty$ chains separated by $|a + c|$ (Fig. 2). The dimensions of the organic ligand molecule are normal, and the two C–O bonds are indistinguishable (Table III).

The coordination geometry about the Cu(I) atom is appoximately tetrahedral, most of the asymmetry

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

Cu–Cl	2.316(3)	Cu–Cl^{a}	2.488(3)
Cu–Cl^{b}	2.392(3)	Cu–N	1.995(7)
N–C(1)	1.35(1)	N–C(5)	1.35(1)
C(1)–C(2)	1.37(1)	C(2)–C(3)	1.36(1)
C(3)–C(4)	1.40(1)	C(4)–C(5)	1.35(1)
C(3)–C(6)	1.49(1)	C(6)–O(1)	1.27(1)
C(6)–O(2)	1.27(1)	O(1)...O(2)^{f}	2.61(1)
Cl–Cu–Cl^{a}	105.0(1)	Cl–Cu–Cl^{b}	105.5(1)
Cl^{a}–Cu–Cu^{b}	108.2(1)	Cl–Cu–N	123.0(3)
Cl^{a}–Cu–N	104.5(3)	Cl^{b}–Cu–N	109.9(3)
Cu–N–C(1)	122.8(6)	Cu–N–C(5)	121.3(6)
C(1)–N–C(5)	115.9(7)	N–C(1)–C(2)	123.8(9)
C(1)–C(2)–C(3)	118.6(9)	C(2)–C(3)–C(4)	119.6(8)
C(3)–C(4)–C(5)	117.5(9)	C(4)–C(5)–N	124.7(9)
C(2)–C(3)–C(6)	120.8(9)	C(4)–C(3)–C(6)	119.6(9)
C(3)–C(6)–O(1)	119.3(9)	C(3)–C(6)–O(2)	117.4(9)
O(1)–C(6)–O(2)	123.3(9)	O(6)–O(1)...O(2)^{f}	118.7(9)
C(6)–O(2)...O(1)^{f}	118.0(9)		

Symmetry transformations: $^{a}-x, 1-y, -z$; $^{b}x, -1+y, z$; $^{c}x, 1+y, z$; $^{d}-x, -y, -z$; $^{e}-x, 2-y, -z$; $^{f}1-x, -y, 1-z$.

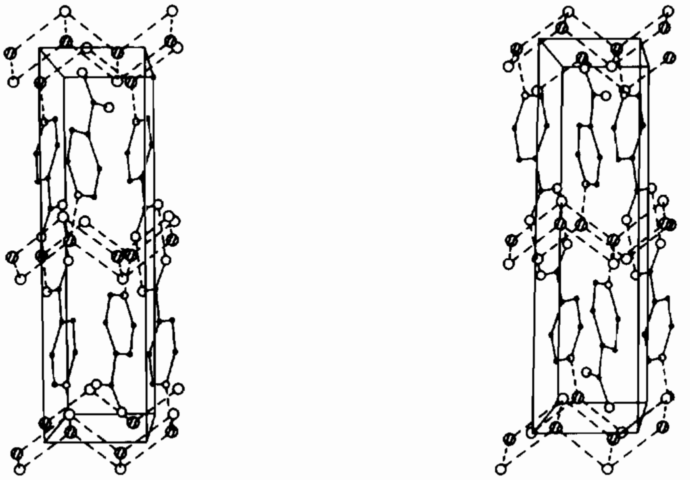

Fig. 2. Stereodrawing of the crystal structure, with metal–ligand bonds represented by broken lines. The unit-cell origin lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards.

being manifested in the large Cl–Cu–N angle (Table III). The organic ligand thus leans away from the shortest of the metal–chloride bonds, namely Cu–Cl = 2.316(3) Å. It is also noted that the longest metal–chloride bond, Cu–Cl^{a} = 2.488(3) Å, constitutes the junction of successive Cu_2Cl_2 units in the polymer string, in agreement with the general pattern observed in other nitrogen–base copper(I) and silver(I) adducts (see Table VI of ref. 15).

References

1 M. A. S. Goher and M. Drátovský, *J. Inorg. Nucl. Chem., 38,* 1269 (1976).

2 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem., 15,* 1155 (1976).

3 T. C. W. Mak, H. N. C. Wong, K. H. Sze and L. Book, *J. Organomet. Chem., 255,* 123 (1983).

4 P. C. Healy, C. Pakawatchai, C. L. Ralston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.,* 1905 (1983).

5 T. C. W. Mak, *Inorg. Chim. Acta, 84,* 19 (1984); *90,* 153 (1984).

6 G. M. Sheldrick, in D. Sayre (ed.), 'Computational Crystallography', Oxford University Press, New York, 1982, p. 506.

7 'International Tables for X-Ray Crystallography, Vol. 4', Kynoch Press, Birmingham, 1974, p. 94, 149.

8 J. A. Campbell, C. L. Ralston and A. H. White, *Aust. J. Chem., 30,* 1937 (1977).

9 E. Eitel, D. Oelkrug, W. Hiller and J. Strahle, *Z. Naturforsch., Teil B:, 35,* 1247 (1980).

10 M. Massaux, M.-J. Bernard and M.-T. Le Bihan, *Bull. Soc. Fr. Mineral. Crystallogr., 92,* 118 (1969).

11 M. Massaux, M. J. Bernard and M. T. Le Bihan, *Acta Crystallogr., Sect. B:, 27,* 2419 (1971).

12 M. Massaux and M. T. Le Bihan, *Acta Crystallogr., Sect. B:, 32,* 1586 (1976).

13 I. D. Brown and J. D. Dunitz, *Acta Crystallogr.; 13,* 28 (1960).

14 F. G. Moers, W. P. J. H. Gosman and P. T. Beurskens, *J. Cryst. Mol. Struct., 2,* 23 (1972).

15 P. C. Healy, N. K. Mills and A. H. White, *Aust. J. Chem., 36,* 1851 (1983).

16 M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta, 99,* 223 (1985).