PREPARATION AND SPECTRAL CHARACTERIZATION OF COPPER(I) HALIDE, NITRATE AND PERCHLORATE COMPLEXES OF PYRAZINIC ACID AND X-RAY CRYSTAL STRUCTURE OF POLYMERIC [Cu₂(PYRAZINIC ACID)₂I₂]·3H₂O

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Abstract—Copper(I) salts formed with pyrazinic acid (pyz-H) complexes of the types $Cu(pyz-H)_2X \cdot 2H_2O$ for X = Cl or Br, $Cu(pyz-H)X \cdot H_2O$ for X = Br, NO_3 or ClO_4 and $Cu_2(pyz-H)_n X_2 \cdot 3H_2O$ where $n = 3$ for X = Cl and $n = 2$ for X = I. The complexes were characterized by elemental analysis, IR and electronic spectra. The overall physical measurements suggest that pyz-H acts as a monodentate ligand in the $Cu(pyz-H)_2X \cdot 2H_2O$ complexes and as a N,O-bidentate neutral ligand in the hydrated 1:1 complexes, whereas $Cu_2(pyz-H)_3Cl_2 \cdot 3H_2O$ contains both types of acid molecules. The structure of the trihydrated copper(I) iodide complex of pyrazinic acid, as determined by X-ray crystallography, contains the asymmetric $Cu_2(pyz-H)_2I_2 \cdot 3H_2O$ units which are linked together forming a stair or ribbon polymeric structure with tetrahedral copper(I) environments. The two pyrazinic acid molecules in the asymmetric unit behave differently; one acid molecule acts as a neutral ligand whereas the other functions as a zwitterion. Both molecules, however, act as monodentate ligands. The neutral pyrazinic acid molecule forms hydrogen bonds with two water molecules and the zwitterion binds the third water molecule through a hydrogen bond of the type N—H···O. The Cu—N distances are 2.053(4) and 2.064(5) Å, the Cu—I bond lengths vary from 2.618(1) to 2.645(1) Å, and the Cu—Cu distance within the cyclic Cu_2I_2 unit is 2.771(1) Å.

Copper(I) halides form complexes with unidentate nitrogen bases that have recently been widely studied structurally. Among the 1:1:1 copper:halide:base complexes, the tetrameric cluster with cubane stereochemistry is familiar; being exemplified by [CuIL]₄ (L = pyridine,[1] piperidine,[2] morpholine[3] and dimethylnicotinamide[4]) and [CuBrL]₄ (L = 2-methylpyridine[5]). In the case of the step structure of the Cu₂X₄ core which is familiar in the adducts with phosphine or arsine bases,[6–8] no nitrogen base analogue has been reported. Instead, a series of polymeric structures are found for which the step might be considered to form the repeating unit. This common polymeric structure, known as a ribbon or stair polymer, is exemplified by [CuX]∞ adducts with pyridine,[9] isonicotinic acid,[10] methyl cyanide,[11,12] benzonitrile[13] and azomethane.[14]

It was pointed out[15] that picolinic acid, also known as pyridine-2-carboxylic acid, does not form

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complexes with copper(I) salts. Moreover, it was found that it oxidizes copper(I) complexes of some other ligands giving rise to copper(II) species. On the other hand, nicotinic acid,[16] pyridine-3-car-boxylic acid, as well as isonicotinic acid,[10] pyridine-4-carboxylic acid, form with copper(I) halides complexes of the types $[CuXL_2]_\infty$ and $[CuXL]_\infty$, respectively. In the nicotinic acid complex the $(CuCl)_\infty$ chains take the place of the Cu_2Cl_2 stair or ribbon in the isonicotinic adduct. Pyrazinic acid (hereafter abbreviated as pyz-H) combines the coordinating features of the pyridine-2-carboxylic acid in addition to the fact that the pyrazine moiety may act as a bridge and thus aid the formation of poly-meric derivatives.[17] As the complexes of pyrazinic acid with copper(I) had not been reported in the literature, it seemed interesting to study its ability to form such complexes as compared with the above pyridine monocarboxylic acids. In the present work we report on the preparation and characterization of copper(I) complexes of pyrazinic acid together with the X-ray structure analysis of the title complex for which suitable crystals were obtained.

EXPERIMENTAL

Pyrazinic acid was obtained from Aldrich Company and other chemicals were of analytical grade quality.

Preparation of the complexes

Cu(pyz-H)$_2$X · 2H$_2$O *complexes,* X = Cl *or* Br. A boiled acetone solution of pyrazinic acid (5 mmol) was mixed with a suspension of CuX (X = Cl or Br, 2 mmol) in acetone. The mixture was boiled for several minutes. The clear solution was then allowed to stand for several hours (for chloride) or days (for bromide) to produce reddish fine crystals of the complex. The chloride complex was, alternatively, prepared according to the procedure given for the iodide complex.

Cu$_2$(pyz-H)$_3$Cl$_2$ · 3H$_2$O. CuCl$_2$ · 2H$_2$O (2 mmol) in water was reduced by L-(+)-ascorbic acid to yield a cuprous chloride precipitate. The subsequent addition of an ethanolic solution of pyrazinic acid (2 mmol) and boiling of the final mixture for several minutes led to the formation of black fine crystals of the complex after about 20 min.

Cu(pyz-H)Br · H$_2$O. To a suspension of CuBr in water, an ethanolic solution of pyrazinic acid was added. The final mixture was boiled until complete dissolution, cooled and then allowed to stand. The complex was precipitated as crystalline powder after several hours.

Cu(pyz-H)X · H$_2$O, X = NO$_3$ *or* ClO$_4$. These complexes were obtained by addition of excess L-(+)-ascorbic acid to a mixture of Cu(NO$_3$)$_2$ · 3H$_2$O or Cu(ClO$_4$)$_2$ · 6H$_2$O and pyrazinic acid in aqueous/ethanol medium, boiling, cooling and allowing to stand for several hours.

Cu$_2$(pyz-H)$_2$I$_2$ · 3H$_2$O. L-(+)-Ascorbic acid was added to an aqueous solution mixture of Cu(NO$_3$)$_2$ · 3H$_2$O and NaI. A saturated solution of NaI was then added dropwise until a clear solution was obtained. Upon addition of an ethanolic solution of pyrazinic acid and boiling, a yellow, clear solution was produced. This final mixture was allowed to stand for several days to yield orange-brown crystals of the complex. Alternatively, this complex was produced by mixing a suspension of CuI and pyrazinic acid in acetone, boiling, cooling and allowing to stand for several weeks.

Elemental analysis results of the isolated complexes are given in Table 1.

Spectral data

The electronic spectral data of the complexes measured as solid Nujol mulls and some IR absorption bands are collected in Tables 1 and 2. The experimental procedures and instruments used are as described previously.[18]

X-ray structure analysis of polymeric Cu$_2$(pyrazinic acid)$_2$I$_2$ · 3H$_2$O complex

Intensities were recorded on a Nicolet R3m/V four-circle diffractometer[19] at 18°C, and data collection and processing parameters are summarized in Table 3. The raw intensities were processed with the learnt-profile procedure[20] and an absorption correction was based on a pseudo-ellipsoidal fit to azimuthal scans of selected strong reflections over a range of 2θ values.[21,22]
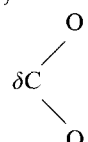
The structure was solved by Patterson superposition and Fourier methods. All non-hydrogen atoms were subjected to anisotropic refinement. The aromatic hydrogen atoms were generated geometrically (C—H fixed at 0.96 Å), allowed to ride on their respective carbon atoms and included in structure-factor calculations with assigned isotropic thermal parameters.

All computations were performed on a DEC Micro VAX-II computer with the SHELXTL-PLUS system.[23,24] Analytical expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[25] Least-squares refinement converged to the R indices and other parameters, as listed in Table 3. Selected bond distances and angles are listed in Table 4. Positional parameters, aniso-

Table 1. Analytical data

Complex	Colour	Found (calc.) (%)					Maximum absorption (nm) (MLCT)	
		C	H	N	Cu	X		
1 $Cu(pyz-H)_2Cl \cdot 2H_2O$	Red-brown crystals	30.8 (31.3)	3.0 (3.2)	14.2 (14.1)	16.2 (16.6)	9.7 (9.3)	425	
2 $Cu(pyz-H)_2Br \cdot 2H_2O$	Orange-red fine crystals	27.8 (28.1)	2.9 (2.8)	13.0 (13.1)	14.7 (14.9)	19.1 (18.7)	415	
3 $Cu_2(pyz-H)_2I_2 \cdot 3H_2O$	Orange-brown crystals	17.5 (17.6)	2.0 (2.1)	8.0 (8.2)	18.2 (18.6)	36.5 (37.2)	400	
4 $Cu_2(pyz-H)_3Cl_2 \cdot 3H_2O$	Black fine needles	28.5 (28.9)	3.0 (2.9)	13.0 (13.2)	20.0 (20.4)	11.0 (11.7)	400	530
5 $Cu(pyz-H)Br \cdot H_2O$	Dark brown fine needles	21.4 (21.0)	2.0 (2.1)	10.0 (9.8)	22.2 (22.3)		400	545
6 $Cu(pyz-H)(NO_3) \cdot H_2O$	Brown fine cryst. powder	23.0 (22.4)	2.3 (2.3)	14.9 (15.7)	24.0 (24.6)		370	520
7 $Cu(pyz-H)(ClO_4) \cdot H_2O$	Dark brown cryst. powder	21.4 (20.9)	2.2 (2.1)	9.5 (9.8)	22.6 (22.1)		350	480

Table 2. IR spectral data for pyrazinic acid and its copper(I) complexes

pyz-H	1	3	6	Assignments
2450 vs, br	3500 s, br, 3140 s	3420 vs, br	3360 s, br	$v(O—H \cdots O) + v(N—H \cdots O)$
	2480 s, br	2600–	2600–	
1800 s, br	2000 ms, br	2300 m	2000 m	
1725 s, br	1700 vs, br	1730 m, br	1770 vs	$v(C=O)$
	1640 vs	1625 ms, br		$v(COO^-)_{asym}$
1580 wm	1588 s	1580 ms	1595 ms	Pyrazine ring vibrations
1440 wm	1448 ms	1450* m	1465 wm	
1390 s	1410 s	1400 s	1410 vs	
1310 vs	1365 s	1365 vs	1360 s	
	1310 vs, br	1330 s, br	1330 vs	$v(C—O) + v(COO)_{sym}$
1265 s		1280 m	1280 m	
1045 vs	1055 s	1055 s	1060 s	Ring breathing
1010 vs	1025	1025 s	1030 s	
690 ms	705 ms	710 m	720 m	$\delta C \begin{smallmatrix} O \\ \\ O \end{smallmatrix}$
485 m	520 s	515 m	525 m	Ring vibrations
425 m	440 ms	445 m	455 m	

v, very; m, medium; s, strong; w, weak; br, broad; *, split band.

tropic thermal parameters, hydrogen atom coordinates, a full list of bond lengths and angles and observed and calculated structure factors have been deposited with the Editor as supplementary material; copies are available on request.

RESULTS AND DISCUSSION

The reactions between pyrazinic acid and copper(I) halide, nitrate and perchlorate or the reduction of copper(II)–pyrazinic acid in the pres-

Table 3. Data collection and processing parameters

Molecular formula	$C_{10}H_{14}N_4O_7Cu_2I_2$
Molecular weight	683.1
Colour and habit	Yellow-brown rectangle
Crystal size (mm^3)	$0.12 \times 0.16 \times 0.25$
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell parameters	
$a = 6.813(1)$ Å	$\alpha = 93.44(1)^\circ$
$b = 8.273(1)$	$\beta = 97.05(1)$
$c = 16.719(2)$	$\gamma = 96.19(1)$
$V = 927(1)$ Å^3	$Z = 2$ $F(000) = 644$
Density (calc.) (g cm^{-3})	2.447
Radiation	graphite-monochromatized Mo-K_α, $\lambda = 0.71073$ Å
Standard reflections	$(-1, 0, -3)$; $(-2, 2, -5)$
Intensity variation (%)	± 1.1
R_{int} (from merging of equiv. reflections)	0.0139
Absorption coefficient (mm^{-1})	5.66
Mean μr	0.50
Transmission factors	0.267 to 0.327
Scan type and rate ($^\circ$ min^{-1})	ω-scan ; 3.0–29.3
Scan range	0.80° below $K\alpha_1$ to 0.80° above $K\alpha_2$
Background counting	Stationary counts for one-fifth of scan time at each end of scan range
Collection range	$0 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $-22 \leqslant l \leqslant 22$; $2\theta_{max} = 57^\circ$
Unique data measured	4738
Obs. data with $|F_o| \geqslant 3\sigma(|F_o|)$, n	3221
No. of variables, p	277
Weighting scheme	$w = [\sigma^2|F_o| + 0.0003|F_o|^2]^{-1}$
$R_F = \Sigma ||F_o| - |F_o||/\Sigma |F_o|$	0.0347
$wR = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$	0.0439
$S = [\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$	1.48
Largest and mean Δ/σ	0.054, 0.002
Residual extrema in final difference map (e Å^{-3})	$+1.44$ to -0.93

ence of these anions afforded the complexes given in Table 1. The brown copper(I) sulphate complex of pyrazinic acid formed in solution was too unstable to be filtered off. All other complexes are coloured and stable against air oxidation when well dried. The copper(I) halide, nitrate and perchlorate complexes of all types are insoluble in non-polar solvents, e.g. benzene, carbon tetrachloride, toluene, etc., and polar solvents e.g. water, alcohols, acetone, nitrobenzene, chloroform, etc., which is an indication of the polymeric nature of these complexes.

The electronic spectra (Table 1, Fig. 1) of the solid copper(I) complexes mulled in Nujol exhibit strong absorption bands in the visible region, which are undoubtedly due to charge-transfer transitions[26] from Cu^I d^{10} to an empty π^* orbital (MLCT) on pyrazinic acid. The brown to black

complexes (4–7), however, show two such MLCT bands. A similar situation occurs in the bis(arylazo-oximates) of copper(I),[27,28] as well as in bis(2-(phenylazo)pyridine)copper(I) complex,[29] except that the two bands appear at 700–780 nm and 550–580 nm. In a tetrahedral molecular environment, the metal valence d orbitals split into two sublevels, t_2 and e. If the two MLCT bands observed in the spectra of some of the present complexes are due to t_2–π^* (480–550 nm) and e–π^* (350–400 nm), the energy gap between them lie, in the range 8500–6200 cm^{-1}. This difference is much greater than those observed in the cases of the above arylazo oximato or phenylazo pyridine–copper(I) complexes. In copper(I) complexes of bipyridine and related ligands the lowest energy charge-transfer band occurs[30] near 450 nm, whereas those of pyridine and related ligands exhibit an MLCT band around

Table 4. Bond lengths (Å) and bond angles (°)

Cu(1)—Cu(2)	2.771 (1)		Cu(1)—I(1)	2.644 (1)
Cu(1)—I(2)	2.645 (1)		Cu(1)—N(1)	2.053 (4)
Cu(2)—I(1)	2.618 (1)		Cu(2)—I(2)	2.641 (1)
Cu(2)—N(3)	2.064 (5)		N(1)—C(1)	1.347 (6)
N(1)—C(4)	1.345 (6)		N(2)—C(2)	1.338 (7)
N(2)—C(3)	1.338 (6)		C(1)—C(2)	1.366 (8)
C(3)—C(4)	1.375 (7)		C(3)—C(5)	1.535 (7)
C(5)—O(1)	1.292 (7)		C(5)—O(2)	1.199 (6)
N(3)—C(6)	1.324 (6)		N(3)—C(9)	1.333 (6)
N(4)—C(7)	1.345 (7)		N(4)—C(8)	1.330 (6)
C(6)—C(7)	1.393 (8)		C(8)—C(9)	1.397 (7)
C(8)—C(10)	1.508 (7)		C(10)—O(3)	1.251 (7)
C(10)—O(4)	1.209(7)			
Cu(2)—Cu(1)—I(1)	57.8(1)		Cu(2)—Cu(1)—I(2)	58.3(1)
I(1)—Cu(1)—I(2)	116.0(1)		Cu(2)—Cu(1)—N(1)	125.6(1)
I(1) —Cu(1)—N(1)	107.3(1)		I(2)—Cu(1)—N(1)	106.8(1)
Cu(1)—Cu(2)—I(1)	58.7(1)		Cu(1)—Cu(2)—I(2)	58.4(1)
I(1)—Cu(2)—I(2)	117.1(1)		Cu(1)—Cu(2)—N(3)	124.5(1)
I(1)—Cu(2)—N(3)	108.3(1)		I(2)—Cu(2)—N(3)	107.9(1)
Cu(1)—I(1)—Cu(2)	63.5(1)		Cu(1)—I(2)—Cu(2)	63.2(1)
Cu(1)—N(1)—C(1)	121.8(3)		Cu(1)—N(1)—C(4)	122.6(3)
C(1)—N(1)—C(4)	115.6(4)		C(2)—N(2)—C(3)	115.8(4)
N(1)—C(1)—C(2)	121.9(5)		N(2)—C(2)—C(1)	122.5(4)
N(2)—C(3)—C(4)	122.0(4)		N(2)—C(3)—C(5)	118.7(4)
C(4)—C(3)—C(5)	119.2(4)		N(1)—C(4)—C(3)	122.0(4)
C(3)—C(5)—O(1)	113.4(4)		C(3)—C(5)—O(2)	119.0(5)
O(1)—C(5)—O(2)	127.6(5)		Cu(2)—N(3)—C(6)	122.1(4)
Cu(2)—N(3)—C(9)	119.9(3)		C(6)—N(3)—C(9)	117.8(5)
C(7)—N(4)—C(8)	116.5(5)		N(3)—C(6)—C(7)	120.9(5)
N(4)—C(7)—C(6)	121.9(4)		N(4)—C(8)—C(9)	121.6(4)
N(4)—C(8)—C(10)	119.6(4)		C(9)—C(8)—C(10)	118.8(4)
N(3)—C(9)—C(8)	121.2(4)		C(8)—C(10)—O(3)	116.6(4)
C(8)—C(10)—O(4)	117.2(5)		O(3)—C(10)—O(4)	126.2(5)
O(1W)—N(2)	2.555		N(2)—H(2N)···O(1W)	146.0
O(2W)—O(4)	2.740		O(2W)—H(2WB)···O(4)	161.3
O(3W)—N(4)	2.912		O(3W)—H(3WA)···N(4)	146.4

380–500 nm.[31–33] In grossly planar and unsaturated macrocyclic environments for copper(I), an allowed transition is documented[34] near 700 nm.

The IR spectra (Table 2) of $Cu(pyz-H)_2X \cdot 2H_2O$ exhibit two bands around 1700 and 1640 cm^{-1} associated with the $v(C=O)$ and $v(COO^-)$, respectively. Thus the $v(C=O)$ band in free pyz-H is a little shifted to lower frequencies in these complexes. This small shift is similar to that observed in Cu(nicotinic acid)$_2$X complexes.[16] The other $v(COO)$ band suggests the presence of a zwitterion form of pyz-H as found for [Co(nicotinate)$_2$(H$_2$O)$_4$].[35] These complexes, therefore, contain a neutral pyrazinic acid molecule as well as a zwitterion molecule. The two water molecules are most likely hydrogen bonded to these two different pyz-H molecules. The existence of O—H···O and

N—H···O bonds are indicated by the strong absorption bands in the region 3500–2000 cm^{-1}.[36] The $Cu_2I_2(pyz)_2 \cdot 3H_2O$ complex exhibits $v(C=O)$ and $v_{as}(COO)$ bands at 1725 and 1530 cm^{-1}, respectively, and strong bands in the region 3500–2000 cm^{-1} due to hydrogen-bonded water molecules. The IR spectrum of the black $Cu_2(pyz-H)_3Cl_2 \cdot 2H_2O$ complex shows two very strong absorption bands at 1670 [$v(C=O)$] and 1640 cm^{-1} [$v(COO)$]. This result suggests that the complex contains two types of pyrazinic acid molecules; a neutral molecule acting as a bidentate ligand, coordinating through its heterocyclic nitrogen and α-carboxy group giving rise to chelate ring with copper(I) atom, and two zwitterions acting as monodentate ligands. Complexes of the type $Cu(pyz-H)X \cdot H_2O$, show only one band around 1660 cm^{-1} [$v(C=O)$],
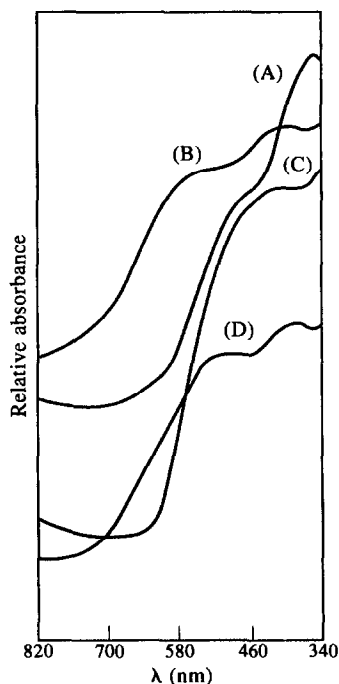
Fig. 1. Electronic spectra of: (A) Cu(pyz-H)ClO$_4$·H$_2$O; (B) Cu$_2$(pyz-H)$_3$Cl$_2$·3H$_2$O; (C) Cu(pyz-H)$_2$Cl·2H$_2$O; (D) Cu(pyz-H)(NO$_3$)·H$_2$O.

suggesting the presence of only bidentate chelating pyrazinic acid molecules.

In the far IR spectra (400–200 cm^{-1}) of the copper(I) chloride or bromide complexes of pyrazinic acid no bands could be attributable to terminal v(Cu—X), which suggests bridging halides are present in such complexes. For the Cu(pyz-H)$_2$X·2H$_2$O complexes, we may assume a polymeric struc-

ture corresponding to that of the 1:2 copper(I) chloride adduct of nicotinic acid having the zigzag (CuCl)$_x$ chain. The Cu$_2$(pyz-H)$_3$Cl$_2$·3H$_2$O may contain discrete dimeric molecules with one bidentate neutral ligand coordinating a copper(I) atom whereas two monodentate zwitterion ligands link the second copper atom. For the Cu(pyz-H)X·H$_2$O complexes with N,O-bidentate pyz-H, we may assume dimeric or polymeric structures corresponding to those of copper(I) iodide complexes of quinaldic acid esters having a chain of alternating copper and iodine atoms or planar Cu$_2$I$_2$ rhombohedra.[37] In the case of the Cu(pyz-H)(ClO$_4$)·H$_2$O complex, the bridging bidentate nature of the perchlorato group is indicated by the appearance of three bands at 1150, 1120 and 1080 cm^{-1} in the v_3 region.[38] Likewise, the appearance of strong bands at 1460 and 1285 cm^{-1} due to v_5 and v_1, respectively, of the NO$_3^-$ group is suggestive of a bridging bidentate nitrate group in the Cu(pyz-H)(O$_3$)·H$_2$O complex. The above conclusions are confirmed by crystal structure determination of the trihydrated copper(I) iodide complex.

The structure determination of the title complex confirms a ribbon or stair polymer chain of edge-sharing Cu$_2$I$_2$ parallelograms propagating in the direction of the short b axis (Figs 2 and 3). 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[9] and Cu(py)I,[9] adducts of CuX (X = Cl, Br, I) with acetonitrile,[11,12] benzonitrile,[13] azomethane,[14] isonicotinic acid[10] and 3-methylrhodamine[39] and adducts of AgI with 2- and 3-methylpyridine and quinoline.[40]
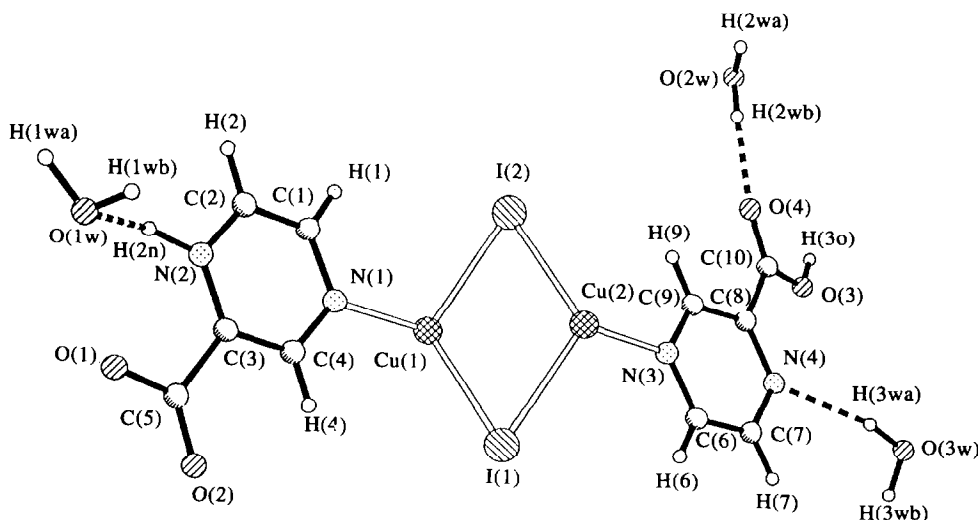

Fig. 2. Atom labelling and principle structural features of polymeric Cu$_2$(pyz-H)$_2$I$_2$·3H$_2$O. Hydrogen bonds are represented by broken lines.
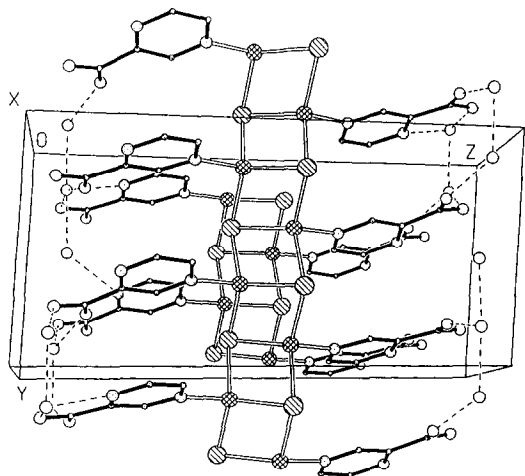
Fig. 3. Stereoview of the crystal structure. Hydrogen bonds are represented by broken lines.

The asymmetric unit, which corresponds exactly to the formula $Cu_2I_2(pyz-H)_2 \cdot 3H_2O$, contains two different pyrazinic acid molecules. While both acid molecules coordinate the copper atoms via the heterocyclic nitrogen only, one of them takes the zwitterionic form with the carboxy proton transferred to N(2), whereas the other molecule remains in the neutral form. The N—H group of the zwitterion forms a hydrogen bond of the type N—H $\cdots$ O with a water molecule. The other two water molecules link the neutral pyrazinic acid through hydrogen bonds of the types O—H $\cdots$ O and O—H $\cdots$ N. The Cu—N bond lengths of 2.053(4) and 2.064(5) Å are a little longer than the corresponding values [2.020(8) and 2.044(9) Å] and 1.995(7) Å found in the structures of [Cu(nicotinic acid)$_2$Cl]$_x$,[16] and [Cu(isonicotinic acid)Cl]$_\infty$,[10] respectively. The Cu—I distances in the present structure (Table 4) are shorter than those usually observed for [CuIL]$_4$ cubes or polymeric pleated sheets where each copper atom has three iodine neighbours [average 2.698(3)[41] and 2.706(3) Å,[42] respectively], but longer than those observed [2.555(1), 2.599(1) Å] in [Cu(2-benzoyl-pyridine)I]$_2$[43] or [2.388(3) Å][44] in CuI$_2^-$ where copper has two neighbours (both iodine) and presumably exhibits multiple bonding character. While three Cu—I distances are equal within experimental error and the fourth Cu—I is a little shorter within the rhombohedron in the present structure, three different Cu—I distances are observed in polymeric pleated sheets, e.g. 2.646(4), 2.681(4), 2.806(4) and 2.644(3), 2.675(2), 2.782(3) Å in [CuI(2-Mepy)]$_\infty$ and [CuI(2,4-Me$_2$py)]$_\infty$, respectively.[42] The Cu $\cdots$ Cu separation of 2.771(1) Å found for the present complex is longer than those observed

in other Cu_2I_2 rhombohedra, e.g. 2.578(1) Å in [CuI(2-benzoylpyridine)]$_2$,[43] 2.544(2) Å in [CuI (isopropylquinaldate)]$_2$,[37] but shorter than 3.706(5) and 3.606(4) Å in [CuI(2-Mepy)]$_\infty$ and [CuI(2,4-Me$_2$py)]$_\infty$,[42] respectively.

Somewhat surprisingly, in the present structure while the difference between C=O and C—O(H) in the neutral pyrazinic acid molecule is 0.042 Å, the two C—O bonds of the carboxy group in the zwitterion differ by 0.093 Å. The corresponding differences observed in the complexes [M(nicotinate)$_2$(H$_2$O)$_4$] (M = Zn and Cr), in which the zwitterionic form of the nicotinate exists, are only 0.03 and 0.037 Å, respectively.[45] In these latter complexes, however, both carbonyl oxygen atoms are hydrogen bonded to water oxygens. The C—O(H) bond length of 1.251(7) Å in the neutral molecule may be compared with the C—O(Mn) distance [1.258(4) Å] found in the structure of [NaMn(py-razinato)(N$_3$)$_2$(H$_2$O)$_2$] where the pyrazinato anion functions as a chelate bidentate ligand.[46] In this manganese(II) complex the difference between the two C—O bonds is only 0.027 Å. Thus, the coordination of the pyrazinato ligand in this complex has only a little effect on the C—O distances of the carboxy group as compared with the non-coordinated COOH group.

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