Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.13491 (7) | 0.27353 (5) | 0.35676 (4) | 0.0441 (2) |
| Br2 | 0.54997 (8) | 0.14313 (5) | 0.25117 (4) | 0.0474 (2) |
| Cu1 | 0.41313 (8) | 0.17649 (5) | 0.40608 (5) | 0.0353 (2) |
| N1 | 0.5548 (6) | 0.3027 (4) | 0.4481 (3) | 0.0384 (11) |
| N2 | 0.3818 (6) | 0.1730 (4) | 0.5501 (3) | 0.0372 (11) |
| N3 | 0.3038 (5) | 0.0333 (3) | 0.4208 (3) | 0.0361 (11) |
| C1 | 0.6547 (8) | 0.3607 (5) | 0.3924 (5) | 0.054 (2) |
| C2 | 0.7476 (9) | 0.4428 (5) | 0.4309 (6) | 0.066 (2) |
| C3 | 0.7387 (9) | 0.4644 (5) | 0.5303 (6) | 0.068 (2) |
| C4 | 0.6388 (8) | 0.4052 (5) | 0.5872 (5) | 0.056 (2) |
| C5 | 0.5478 (7) | 0.3241 (4) | 0.5458 (4) | 0.0428 (15) |
| C6 | 0.4409 (8) | 0.2542 (5) | 0.6033 (4) | 0.054 (2) |
| C7 | 0.2948 (7) | 0.0914 (5) | 0.5890 (4) | 0.046 (2) |
| C8 | 0.2536 (6) | 0.0108 (4) | 0.5134 (4) | 0.0369 (14) |
| C9 | 0.1677 (7) | −0.0798 (5) | 0.5344 (4) | 0.044 (2) |
| C10 | 0.1290 (7) | −0.1493 (5) | 0.4591 (5) | 0.049 (2) |
| C11 | 0.1792 (7) | −0.1267 (5) | 0.3653 (5) | 0.048 (2) |
| C12 | 0.2657 (7) | −0.0348 (4) | 0.3484 (4) | 0.0421 (14) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—Cu1 | 2.612 (1) | C1—C2 | 1.381 (8) |
| Br2—Cu1 | 2.412 (1) | C2—C3 | 1.374 (9) |
| Cu1—N2 | 1.966 (4) | C3—C4 | 1.348 (9) |
| Cu1—N3 | 2.041 (5) | C4—C5 | 1.379 (8) |
| Cu1—N1 | 2.045 (5) | C5—C6 | 1.465 (8) |
| N1—C1 | 1.330 (7) | C7—C8 | 1.484 (8) |
| N1—C5 | 1.349 (7) | C8—C9 | 1.378 (8) |
| N2—C6 | 1.345 (7) | C9—C10 | 1.383 (8) |
| N2—C7 | 1.363 (7) | C10—C11 | 1.366 (8) |
| N3—C12 | 1.340 (7) | C11—C12 | 1.383 (8) |
| N3—C8 | 1.351 (7) | | |
| N2—Cu1—N3 | 79.8 (2) | C8—N3—Cu1 | 114.5 (4) |
| N2—Cu1—N1 | 79.7 (2) | N1—C1—C2 | 122.1 (6) |
| N3—Cu1—N1 | 156.5 (2) | C3—C2—C1 | 119.1 (7) |
| N2—Cu1—Br2 | 157.04 (13) | C4—C3—C2 | 119.0 (6) |
| N3—Cu1—Br2 | 97.09 (13) | C3—C4—C5 | 120.2 (6) |
| N1—Cu1—Br2 | 97.32 (14) | N1—C5—C4 | 121.3 (6) |
| N2—Cu1—Br1 | 98.23 (13) | N1—C5—C6 | 115.4 (5) |
| N3—Cu1—Br1 | 95.36 (12) | C4—C5—C6 | 123.3 (6) |
| N1—Cu1—Br1 | 98.86 (12) | N2—C6—C5 | 112.9 (5) |
| Br2—Cu1—Br1 | 104.72 (3) | N2—C7—C8 | 112.1 (5) |
| C1—N1—C5 | 118.4 (5) | N3—C8—C9 | 121.7 (5) |
| C1—N1—Cu1 | 128.0 (4) | N3—C8—C7 | 115.1 (5) |
| C5—N1—Cu1 | 113.6 (4) | C9—C8—C7 | 123.3 (5) |
| C6—N2—C7 | 124.2 (5) | C8—C9—C10 | 119.7 (5) |
| C6—N2—Cu1 | 117.5 (4) | C11—C10—C9 | 118.8 (6) |
| C7—N2—Cu1 | 118.2 (4) | C10—C11—C12 | 119.1 (6) |
| C12—N3—C8 | 118.0 (5) | N3—C12—C11 | 122.7 (5) |
| C12—N3—Cu1 | 127.3 (4) | | |

H atoms were placed in calculated positions, riding on their respective host atom. A disordered model was used for those H atoms attached to C6 and C7, to take account of the high degree of delocalization in the C—N bonds.

Data collection: *P3/P4/PC* (Siemens, 1991). Cell refinement: *P3/P4/PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL93*; *PARST93* (Nardelli, 1983).

The authors would like to thank Fundacion Andes for the purchase of the single crystal diffractometer currently operating at the Universidad de Chile, and Fondecyt (1940515) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Dichloro(di-2-pyridylamine-*N*,*N*′)copper(II)

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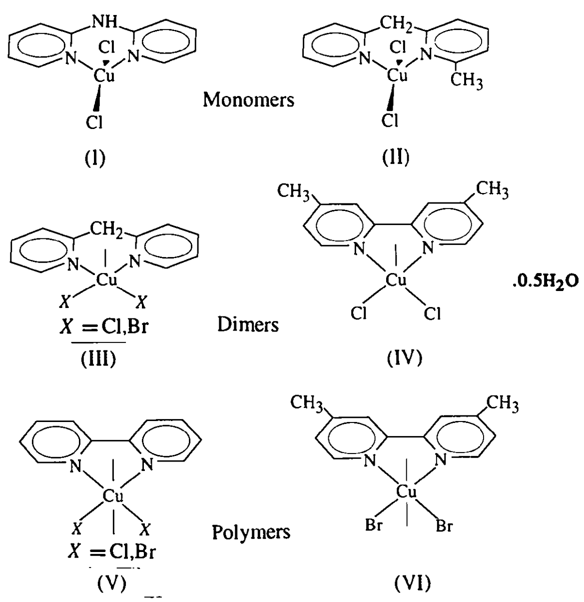
## Abstract

The title complex, $[CuCl_2(C_{10}H_9N_3)]$, is a monomer, with the Cu atom in a rather distorted tetrahedral environment provided by two $Cl^-$ ions and two N atoms from the bidentate bipyridine derivative. The group is bisected by a twofold axis passing through the cation and the amine N atom bridging the symmetry-related pyridine groups. The deformation of the coordination tetrahedron is due to the $Cl^-$ ion taking part in intramolecular interactions.

## Comment

Copper(II) complexes of formula $[Cu(NN')X_2]$, where $X$ is Cl or Br and $NN'$ is a pyridine derivative, show different geometries with four-, five- and six-fold coordination. These complexes can crystallize as monomers, dimers and different kinds of polymers. Our previous work led to the characterization of a number of 2,2′-bipyridine complex derivatives (see scheme below), namely, dichloro[6-methyl-2-(2-pyridylmethyl)pyridine-*N*,*N*′]copper(II), (II) (Garcia, Manzur, Spodine, Baggio & Garland, 1994), dichloro-(or dibromo)(di-2-pyridylmethane)copper(II), (III) (Spodine, Manzur, Garland, Fackler, Staples & Trzcinska-Bancroft, 1993; Garland, Grandjean, Spodine & Manzur, 1987), dichloro(4,4′-dimethyl-2,2′-bipyridine)copper(II) hemihydrate, (IV) (Gonzalez, Atria, Spodine, Manzur & Garland, 1993), *catena*-di-$\mu$-chloro(or bromo)-(2,2-bipyridine)copper(II), (V) (Garland, Grandjean, Spodine, Atria & Manzur, 1988), and dibromo(4,4′-dimethyl-2,2′-bipyridine)copper(II), (VI) (Atria *et al.*, 1993).



The atomic labelling used for the title compound, (I), is shown in Fig. 1. The complex exists as a monomer, with the Cu atom in a rather distorted tetrahedral environment provided by two $Cl^-$ ions and two N atoms from the bidentate bipyridine derivative. The group is bisected by a twofold axis passing through the cation and the amine N atom bridging the symmetry-related pyridine groups; the pyridine groups are strictly planar [the largest deviation from the least-squares plane is 0.009 (7) Å for atom C3] but are not parallel to the symmetry axis. As a result, the composite group is slightly twisted, with an angle of 7.3 (3)° between the normals to the pyridine planes.

The main distortion of the Cu1 environment from tetrahedral symmetry is due to the fact that the Cl1 ion is engaged in a number of hydrogen bonds of the C—H$\cdots$Cl type (Taylor & Kennard, 1982), both intramolecular [H1*a*$\cdots$Cl1$^{\rm i}$ 2.86 Å and C1—H1*a*$\cdots$Cl1$^{\rm i}$ 115°; symmetry code: (i) $-x$, $y$, $-z$] and intermolecular [H2*b*$\cdots$Cl1$^{\rm ii}$ 2.73 Å and N2—H2*b*$\cdots$Cl1$^{\rm ii}$ 141°, H4*a*$\cdots$Cl1$^{\rm iii}$ 2.85 Å and C4—H4*a*$\cdots$Cl1$^{\rm iii}$ 132°; symmetry codes: (ii) $x$, $y-1$, $z$; (iii) $-x$, $y-1$, $-z$]. The main result is a rotation of the Cl1—Cu—Cl1′ plane around the symmetry axis, driving the dihedral angle it makes with the plane through N—Cu—N′ from the expected value of 90° to a value of 61.3 (1)°.

The intermolecular interactions define infinite chains along the $y$ direction. These chains are, in turn, held together by a weak hydrogen bond along the $z$ direction [H1*a*$\cdots$Cl1$^{\rm iv}$ 2.95 Å and C1—H1*a*$\cdots$Cl1$^{\rm iv}$ 119°; symmetry code: (iv) $-x$, $y$, $-1-z$], as well as the usual van der Waals forces.

The bite parameter, as described by Lippard (1967), Drew (1977), Kepert (1977, 1978) and Favas & Kepert (1980), is 94.6 (2) for (I), 89.7 for (II), 85.8 for (III) ($X$ = Cl), 86.2 for (III) ($X$ = Br), 80.2 for (IV) and 79.4° for (VI). The largest values are found for the tetrahedral coordination, which only generates monomeric species. Polymeric structures exhibit smaller values of the bite parameter, while the dimers do not show a definite trend.

In the case of the present complex, the NH group of the di-2-pyridylamine ligand shows a bridging angle of 135°, which generates the largest bite parameter and determines the tetrahedral geometry.

The different molecular structures of compounds (II) and (III), which contain the same heterocyclic ligand, are due to steric hindrance shown by the methyl group and the halogen atom of compound (II). This steric

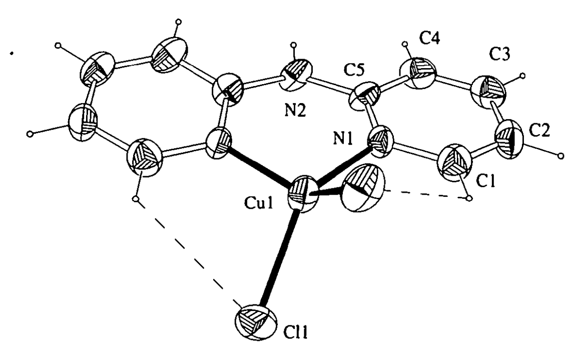


Fig. 1. View of the title molecule showing the atom-labelling scheme, as well as the intramolecular hydrogen bonds. Displacement ellipsoids are shown at the 50% probability level.

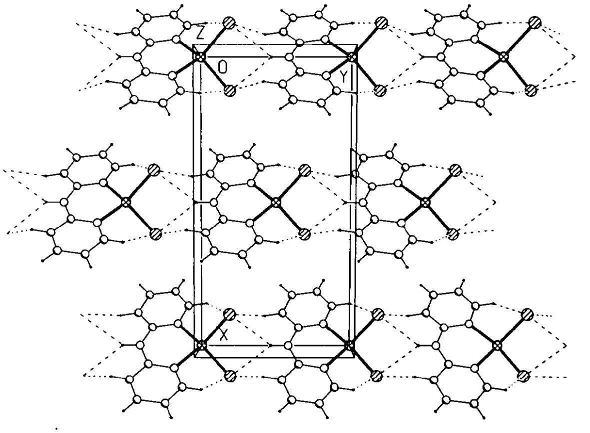


Fig. 2. A packing diagram viewed along the $z$ axis.

hindrance inhibits the formation of the planar unit around the metal center seen in compound (III), where the existence of this unit permits dimer formation.

## Experimental

The title compound was prepared by mixing equimolar quantities of $CuCl_2.2H_2O$ and di-2-bipyridylamine in ethanol. The resultant solution was refluxed for 30 min. After a week, well developed but poorly diffracting crystals were obtained, which were used for data collection.

### *Crystal data*

$[CuCl_2(C_{10}H_9N_3)]$
$M_r = 305.64$
Monoclinic
$C2$
$a = 14.664\,(13)$ Å
$b = 7.697\,(8)$ Å
$c = 5.080\,(5)$ Å
$\beta = 96.71\,(1)°$
$V = 569.4\,(10)$ Å$^3$
$Z = 2$
$D_x = 1.783$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–12.5°$
$\mu = 2.359$ mm$^{-1}$
$T = 293\,(2)$ K
Platelet
0.90 × 0.14 × 0.02 mm
Deep blue

### *Data collection*

Siemens $R3m$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
  $\psi$ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
  $T_{min} = 0.82$, $T_{max} = 1.00$
563 measured reflections
405 independent reflections
396 observed reflections
  $[I > 2\sigma(I)]$

$R_{int} = 0.0344$
$\theta_{max} = 22.47°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = -1 \rightarrow 5$
2 standard reflections
  monitored every 98 reflections
  intensity decay: none

### *Refinement*

Refinement on $F^2$
$R(F) = 0.0377$
$wR(F^2) = 0.0886$
$S = 1.148$
405 reflections
73 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.962$ e Å$^{-3}$
$\Delta\rho_{min} = -0.455$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0 | 0 | 0 | 0.0363 (5) |
| Cl1 | 0.1121 (2) | 0.1910 (3) | −0.0581 (4) | 0.0479 (7) |
| N1 | −0.0699 (3) | −0.1717 (9) | −0.2217 (10) | 0.0283 (14) |
| N2 | 0 | −0.4147 (12) | 0 | 0.034 (2) |
| C1 | −0.1273 (5) | −0.1101 (13) | −0.4288 (15) | 0.042 (2) |
| C2 | −0.1732 (5) | −0.2105 (15) | −0.6157 (14) | 0.041 (2) |
| C3 | −0.1619 (5) | −0.3913 (14) | −0.5960 (15) | 0.040 (2) |
| C4 | −0.1032 (5) | −0.4557 (12) | −0.3909 (15) | 0.042 (2) |
| C5 | −0.0572 (5) | −0.3465 (11) | −0.2044 (14) | 0.033 (2) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Cu1—N1 | 1.948 (6) | C1—C2 | 1.343 (12) |
| Cu1—Cl1 | 2.250 (3) | C2—C3 | 1.40 (2) |
| N1—C1 | 1.354 (10) | C3—C4 | 1.364 (12) |
| N1—C5 | 1.360 (11) | C4—C5 | 1.382 (12) |
| N2—C5 | 1.361 (8) | | |
| N1—Cu1—Cl1 | 135.3 (2) | C4—C3—C2 | 118.3 (8) |
| C1—N1—C5 | 117.7 (7) | C3—C4—C5 | 121.1 (8) |
| C1—N1—Cu1 | 116.7 (6) | N1—C5—N2 | 119.9 (7) |
| C5—N1—Cu1 | 125.1 (5) | N1—C5—C4 | 120.3 (7) |
| C2—C1—N1 | 124.3 (9) | N2—C5—C4 | 119.8 (8) |
| C1—C2—C3 | 118.3 (7) | | |

The data were collected using a variable scan speed of 4.19–29.3° min$^{-1}$ and corrected for absorption. The ratio of maximum to minimum transmission factors output by the $\psi$-scan procedure was underestimated as compared with estimates from crystal size and absorption coefficient, probably due to the pure quality of the azimuthal data used for the correction. The structure was solved through a combination of direct methods and difference Fourier synthesis. Refinement was performed on $F^2$, using the whole data set. H atoms were included at their expected positions, with fixed displacement parameters.

Data collection: *P3/P4/PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4/PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93 and *PARST* (Nardelli, 1983).

The authors would like to thank Fundacion Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile, and Fondecyt (1940515) for financial support.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1211). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Bis(pyridine-2,3-dicarboxylato-*N*,*O*)-copper(II)

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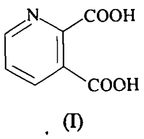
(*Received 31 October 1995; accepted 24 January 1996*)

## Abstract

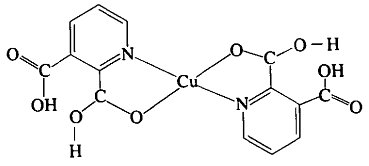
The coordination geometry of the Cu atom in the title compound, $[Cu(C_7H_5NO_4)_2]$, is distorted octahedral and the molecule displays crystallographic inversion symmetry. The Cu atom is bonded to a carboxylate O atom (at the pyridine 2 position) and the pyridine N atom of two ligands, the four atoms forming the equatorial plane, and *via* weaker axial contacts to two carboxylic acid O atoms (at the pyridine 3 position) of adjacent molecules. Strands of molecules are thus linked parallel to the $x$ axis and hydrogen bonds link the strands parallel to the $y$ axis.

## Comment

Pyridine-2,3-dicarboxylic acid, (I), also known as quinolinic acid, is a neurotoxic tryptophan metabolite, a precursor of nicotinamide adenine dinucleotide, and an agonist of the *N*-methyl-D-aspartate receptor (Kalish, Jhamandas, Boegman & Beninger, 1994; Espey, Moffett & Namboodiri, 1995; Mawatari, Oshida, Iinuma & Watanabe, 1995). Its anion forms chelate complexes with Mn, Co, Ni and Zn; the crystal structures of the complexes with Ni and Mn have been reported previously (Goher, Youssef, Zhou & Mak, 1993). It is important to determine the precise crystal structure of the various metal complexes of quinolinic acid and its anions in order to relate the effects of this metabolite and/or related compounds on many physiological processes involving metal enzymes. The crystal structure of quinolinic acid itself has been determined by both X-ray analysis (Takusagawa, Hirotsu & Shimada, 1973) and neutron analysis (Kvick, Koetzle, Thomas & Tagusagawa, 1974; Takusagawa & Koetzle, 1978). We report herein the structure of bis(pyridine-2,3-dicarboxylato-*N*,*O*)copper(II), (II).



(I)



(II)

The molecular structure of (II) is shown in Fig. 1. The Cu atom displays distorted octahedral geometry. It lies on an inversion centre, bonded to two pyridine N atoms [Cu(1)—N(1) 1.969 (3) Å] and two carboxylate O(1) atoms of the carboxylate groups in the pyridine 2 positions [Cu(1)—O(1) 1.926 (3) Å], which form the equatorial plane. It is bonded more weakly to two O(4) atoms of the carboxylic acid groups at the pyridine 3 positions of adjacent molecules [Cu(1)···O(4)($-1+x$, $y$, $z$) and Cu(1)···O(4)($1-x$, $-y$, $1-z$) 2.660 (3) Å] in the axial directions. The carboxylate group in position 2 is almost parallel to the pyridine ring plane [O(1)—

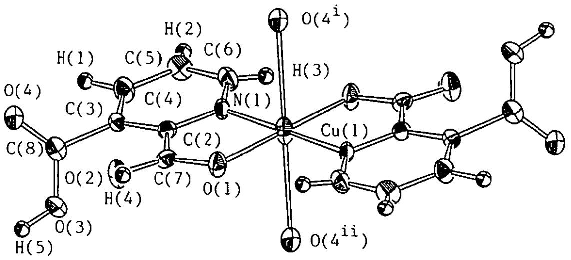


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids correspond to 50% probability and H atoms are drawn as circles of arbitrary radii. [Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $-1+x$, $y$, $z$.]

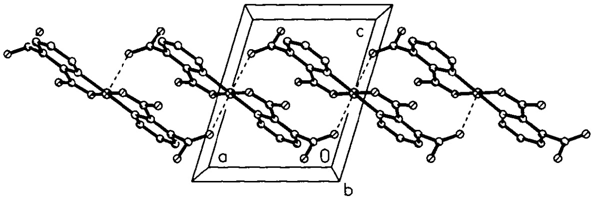


Fig. 2. A view of the weak axial contacts (dashed lines) linking molecules parallel to the $x$ axis.