due to chelation of the two dtc ligands. Thus the Sn atom is six-coordinated in a distorted octahedral arrangement by the ester group [C(1)], the Cl atom, and the chelating dtc residues [S(1), S(2), S(3), and S(4)], with the C(1) and Cl occupying mutually *cis* positions [C(1)—Sn—Cl, 93·6 (3)°]. Typically small bite angles [S(1)—Sn—S(2), 69·6 (1); S(3)—Sn—S(4), 69·7 (1)°] of the dtc ligands are in part responsible for the distortion of the geometry. The Sn—C(1) [2·188 (10) Å] and Sn—Cl [2·458 (3) Å] bond distances in the title compound are slightly longer than those [Sn—C(1), 2·121 (7); Sn—Cl, 2·428 (2) Å] of the monodithiocarbamate analog probably owing to relatively low Lewis acidity of the Sn atom due to the partial change of the donor atoms.

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Structure of (2,2′-Bipyridine-3,3′-dicarboxylic acid)dichlorocopper(II) Monohydrate

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Abstract. $[CuCl_2(C_{12}H_8N_2O_4)].H_2O$, $M_r = 396{\cdot}7$, orthorhombic, *Pbca*, $a = 9{\cdot}932\ (1)$, $b = 17{\cdot}560\ (2)$, $c = 17{\cdot}065\ (2)$ Å, $V = 2976{\cdot}2\ (6)$ Å^3, $Z = 8$, $D_x = 1{\cdot}77$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 18{\cdot}54$ cm^{-1}, $F(000) = 1592$, $T = 291$ K, final $R = 0{\cdot}034$ for 2543 unique observed reflections. The coordination of the Cu atom is approximately square planar with the two Cl atoms and the two N atoms of the bipyridyl ligand occupying the four coordination sites. There is an additional weak interaction between the Cu atom and the Cl and carboxylic acid carbonyl O atoms on neighbouring molecules, resulting in an approximately octahedral arrangement of ligands around the metal atom. The uncoordinated carboxylic acid groups and the water molecules form an intermolecular hydrogen-bonding network throughout the structure.

Introduction. While there are numerous studies involving the metal complexes of 2,2′-bipyridine and related ligands (McWhinnie & Miller, 1969; Fronczek, Gupta & Newkome, 1983; McMillin, Kirchoff & Goodwin, 1985), much less is known about the complexes of functionally substituted bipyridines. We are interested in the possibility of synthesizing polynuclear metal complexes with 2,2′-bipyridine-3,3′-dicarboxylic acid. However, the reaction of this ligand with copper(II) chloride resulted in the (mononuclear) title complex (1). We undertook the crystal structure determination in order to establish the nature of the complex, in particular the mode of coordination of 2,2′-bipyridine-3,3′-dicarboxylic acid to the Cu atom.

Experimental. 2,2′-Bipyridine-3,3′-dicarboxylic acid was prepared by the permanganate oxidation of 1,10-phenanthroline (Wimmer & Wimmer, 1983). A green precipitate is immediately obtained when aqueous solutions of the ligand and copper(II) chloride are mixed together in molar ratio. Upon

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Table 1. *Atomic fractional coordinates and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Cu	0·0403 (1)	0·0925 (1)	0·0619 (1)	0·035 (1)
Cl(1)	0·0377 (1)	0·0714 (1)	0·1938 (1)	0·051 (1)
Cl(2)	−0·1596 (1)	0·0358 (1)	0·0434 (1)	0·046 (1)
O	0·1592 (4)	0·4332 (2)	0·2565 (2)	0·074 (2)
O(1)	0·3987 (2)	0·2795 (1)	−0·0839 (1)	0·045 (1)
O(2)	0·3069 (3)	0·3133 (2)	−0·1980 (1)	0·057 (2)
O(3)	0·5944 (2)	0·1255 (2)	−0·1252 (1)	0·058 (2)
O(4)	0·3875 (2)	0·1193 (1)	−0·1729 (1)	0·047 (1)
N(1)	0·0508 (2)	0·1428 (1)	−0·0435 (1)	0·032 (1)
N(2)	0·2393 (2)	0·1190 (1)	0·0600 (1)	0·032 (1)
C(1)	−0·0578 (3)	0·1613 (2)	−0·0860 (2)	0·041 (2)
C(2)	−0·0501 (3)	0·2102 (2)	−0·1489 (2)	0·047 (2)
C(3)	0·0704 (3)	0·2451 (2)	−0·1643 (2)	0·042 (2)
C(4)	0·1844 (3)	0·2282 (2)	−0·1203 (1)	0·032 (1)
C(41)	0·3090 (3)	0·2744 (2)	−0·1311 (2)	0·036 (2)
C(5)	0·1730 (2)	0·1722 (2)	−0·0621 (1)	0·028 (1)
C(6)	0·2829 (2)	0·1393 (1)	−0·0124 (1)	0·027 (1)
C(7)	0·4167 (3)	0·1248 (2)	−0·0344 (2)	0·030 (1)
C(71)	0·4625 (3)	0·1248 (2)	−0·1180 (2)	0·034 (1)
C(8)	0·5054 (3)	0·0984 (2)	0·0223 (2)	0·038 (2)
C(9)	0·4612 (3)	0·0834 (2)	0·0973 (2)	0·042 (2)
C(10)	0·3270 (3)	0·0920 (2)	0·1129 (2)	0·037 (2)

Table 2. *Selected bond distances* (Å), *bond angles* (°), *torsion angles* (°) *and intermolecular contacts* (Å, °) *with e.s.d.'s in parentheses*

(*a*) Bond distances

Cu—Cl(1)	2·282 (1)	N(1)—C(1)	1·340 (4)	N(1)—C(5)	1·358 (3)
Cu—Cl(2)	2·244 (1)	N(2)—C(6)	1·358 (3)	N(2)—C(10)	1·341 (4)
Cu—N(1)	2·007 (2)	C(1)—C(2)	1·378 (5)	C(9)—C(10)	1·368 (4)
Cu—N(2)	2·032 (2)	C(2)—C(3)	1·370 (4)	C(8)—C(9)	1·379 (4)
C(3)—C(4)	1·392 (4)	C(7)—C(8)	1·389 (4)	C(4)—C(5)	1·402 (4)
C(5)—C(6)	1·499 (3)	C(6)—C(7)	1·405 (4)	C(4)—C(41)	1·491 (4)
C(41)—O(1)	1·206 (3)	C(41)—O(2)	1·330 (4)	C(7)—C(71)	1·497 (4)
C(71)—O(3)	1·317 (4)	C(71)—O(4)	1·202 (3)		

(*b*) Bond angles

Cl(1)—Cu—Cl(2)	93·2 (1)	Cl(2)—Cu—N(1)	96·6 (1)
Cl(1)—Cu—N(1)	163·0 (1)	Cl(2)—Cu—N(2)	163·9 (1)
Cl(1)—Cu—N(2)	93·6 (1)	N(1)—Cu—N(2)	80·5 (1)
Cu—N(1)—C(1)	123·4 (2)	Cu—N(2)—C(10)	122·7 (2)
Cu—N(1)—C(5)	115·1 (2)	Cu—N(2)—C(6)	112·6 (2)
C(1)—N(1)—C(5)	120·1 (2)	C(6)—N(2)—C(10)	119·9 (2)
C(3)—C(4)—C(5)	117·8 (2)	C(8)—C(7)—C(6)	118·4 (2)
C(3)—C(4)—C(41)	119·5 (2)	C(8)—C(7)—C(71)	118·1 (2)
C(5)—C(4)—C(41)	122·5 (2)	C(6)—C(7)—C(71)	122·8 (2)
C(4)—C(41)—O(1)	124·8 (2)	C(7)—C(71)—O(4)	123·7 (2)
C(4)—C(41)—O(2)	111·9 (2)	C(7)—C(71)—O(3)	113·0 (2)
O(1)—C(41)—O(2)	123·2 (2)	O(3)—C(71)—O(4)	123·0 (3)

(*c*) Selected torsion angles

N(1)—C(5)—C(6)—N(2)	−30·1 (2)	C(4)—C(5)—C(6)—C(7)	−35·4 (2)
Cl(2)—Cu—N(1)—C(5)	−167·7 (2)	Cl(1)—Cu—N(2)—C(6)	−177·5 (2)
C(3)—C(4)—C(41)—O(1)	158·8 (2)	C(8)—C(7)—C(71)—O(4)	152·3 (2)

(*d*) Intermolecular distances less than 3·2 Å between non-H atoms

Cu···Cl(2^{i})	3·117 (1)	Cu···O(1^{ii})	2·678 (2)
Cl(1)···O(2^{ii})	3·060 (3)	O···O(3^{ii})	2·549 (4)
O···O(4^{ii})	3·189 (4)	N(1)···O(1^{ii})	2·979 (3)
C(1)···O(1^{ii})	3·111 (4)	O(4)···O^{iii}	2·728 (4)

(*e*) Angles involving intermolecular contacts less than 3·2 Å to the Cu atom

O(1^{ii})···Cu—Cl(1)	89·5 (1)	Cl(2^{i})···Cu—Cl(1)	117·1 (1)
O(1^{ii})···Cu—Cl(2)	85·9 (1)	Cl(2^{i})···Cu—Cl(2)	86·3 (1)
O(1^{ii})···Cu—N(1)	77·5 (1)	Cl(2^{i})···Cu—N(1)	77·4 (1)
O(1^{ii})···Cu—N(2)	108·7 (1)	Cl(2^{i})···Cu—N(2)	77·7 (1)
O(1^{ii})···Cu···Cl(2^{i})	152·6 (1)		

Symmetry operations: (i) $-x, -y, -z$; (ii) $x-0·5, 0·5-y, -z$; (iii) $x, 0·5-y, z-0·5$.

recrystallization from dilute hydrochloric acid green prismatic crystals of (1) are formed. Analytical results (%) with calculated values in parentheses are as follows: C 36·25 (36·33), H 1·92 (2·54), N 8·45 (7·06), Cu 15·80 (16·02), Cl 17·70 (17·87). The crystal chosen for data collection was 0·40 × 0·43 × 0·72 mm. The unit-cell parameters were obtained by a least-squares fit to the θ values of 75 automatically centred reflections ($9·3 < \theta < 23·0°$). Intensity data were measured within the range $1·1 < \theta < 27·8°$ on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation by a θ–2θ scan technique in 48 steps, where the time spent measuring the background was half that taken to measure the peak. The intensity of a reflection and its estimated standard deviation were calculated from $I = \mathrm{INT} - 2(\mathrm{BGL} + \mathrm{BGR})$ and $\sigma(I) = [\mathrm{INT} + 4(\mathrm{BGL} + \mathrm{BGR})]^{0·5}$, where INT, BGL and BGR are the peak intensity, left and right background counts, respectively. The horizontal detector aperture and the ω-scan range varied as $(3·2 + 1·25\tan\theta)$ mm and $(0·8 + 0·35\tan\theta)°$. The intensities of three standard reflections, remeasured every 100 reflections, showed no significant variation during data collection. Data were corrected for Lorentz, polarization and absorption (max. correction 1·14, min. 0·76; Walker & Stuart, 1983). $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{0·5}/2F$, where $k = 0·02$. Of 4025 measured intensities (h −4→11, k −8→20, l 0→20), 2543 had $I > 2·0\sigma(I)$, and only these were used in the solution and refinement of the structure. Computer programs used in this investigation include modified versions of *DATAP* data reduction program (Coppens, Leiserowitz & Rabinovich, 1965), *TRACER* (Jacobson & Lawton, 1965) for cell reduction, *SHELX* (Sheldrick, 1974) for crystal structure solution and refinement, a modified version of *ORFLS* least-squares program for blocked-diagonal refinement (Busing, Martin & Levy, 1962), *DAESD* program for distances and angles (Davis & Harris, 1970), *XANADU* molecular geometry program (Roberts & Sheldrick, 1976) and *ORTEP* thermal-ellipsoid plotting program (Johnson, 1976).

The structure was solved by the heavy-atom method. Refinement was by blocked least-squares methods, where the function minimized was $\sum w(\Delta F)^2$ with $w = 1/\sigma(F)^2$ and $\Delta F = |F_o| - |F_c|$. Refinement of the positional and isotropic thermal parameters of the non-H atoms resulted in $R = 0·107$ ($wR = 0·123$). The positions of the H atoms were located on a difference Fourier map and included in the refinement with isotropic thermal parameters. Refinement converged at $R = 0·034$, $wR = 0·038$, $S = 2·07$ for 239 variables and 2543 reflections. The large S value indicates a slight underestimation of the error of an observation of unit weight. In the final refinement cycle the maximum shift-to-e.s.d. ratio was 1·1 for the thermal parameter of one H atom and below 0·57 for the remaining parameters. Atomic scattering curves were taken from *Interna-*

tional Tables for X-ray Crystallography (1974). Corrections for anomalous dispersion for Cu ($f' = 0·263$, $f'' = 1·266$) and Cl ($f' = 0·132$, $f'' = 0·159$) were those reported by Cromer & Liberman (1970). In the final difference Fourier syntheses, peaks of $\pm 0·42$ e Å^{-3} were observed. Positional parameters are given in Table 1,* and bond lengths, bond angles and selected torsion angles are presented in Table 2.

Discussion. Fig. 1 shows the molecular structure of (1) and Fig. 2 the packing of molecules in the unit cell. The coordination around the Cu atom is approximately square planar with the two Cl atoms and the N atoms of the bipyridyl ligand occupying the four coordination sites. Weak intermolecular interactions with a Cl atom [Cu···Cl 3·117 (1) Å] and an O atom [Cu···O 2·678 (2) Å] on adjacent molecules in the unit cell (Fig. 2, Tables 2*d*,*e*) complete an octahedral arrangement of donor atoms around the metal. The bipyridyl ligand is not planar, presumably as a result of steric interaction between the two carboxylic acid groups, which occupy the 3,3′-positions in the molécule. The planar pyridine rings are thus twisted by about 30° relative to one another around the C(5)—C(6) bond (Table 2*c*). Distances and angles within the bipyridyl ligand are similar to those observed in other complexes containing this ligand (Brauer, Kaiser, Rasmussen, Schröder & Taylor, 1974; Fronczek, Gupta & Newkome, 1983). Whereas one carboxylic acid group is involved in interaction with the Cu atom on a neighbouring atom, the other forms hydrogen bridges to the water of crystallization [H(7)···O 1·79 (4) Å, O(3)—H(7)···O 160 (5)°, H(5)···O(4) 1·98 (4) Å, O—H(5)···O(4) 172 (4)°], which itself acts as a bridge between adjacent molecules (Table 2*d*). We are presently investigating the consequences of the hydrogen-bonding network for the magnetic exchange interactions between the Cu^{2+} sites in this crystal as reflected in its magnetic and magnetic resonance properties.

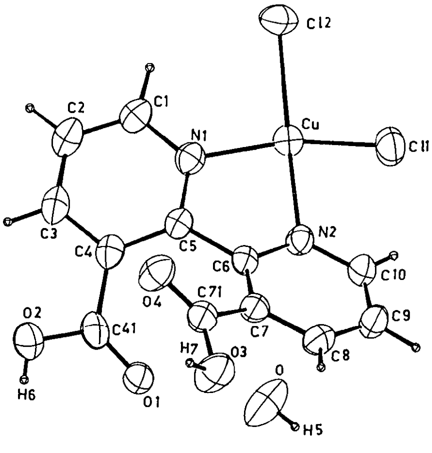

Fig. 1. The molecular structure of (1).

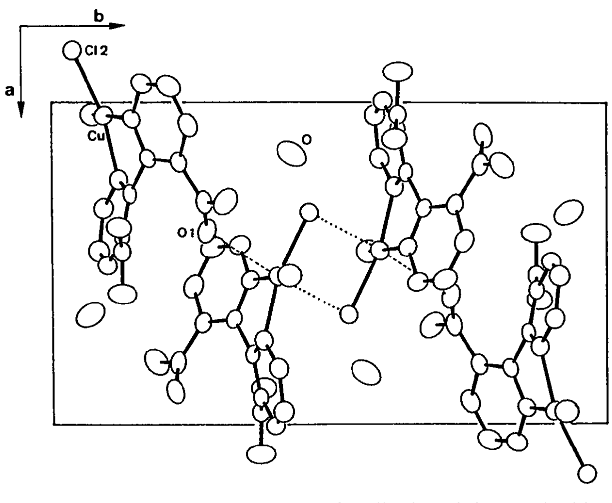

Fig. 2. The packing of (1) in the unit cell, viewed down **c** looking towards the origin. Only four molecules are shown for clarity. The weak interactions between the Cu atom and atoms on adjacent molecules are indicated by dashed (Cu···O) and dotted (Cu···Cl) lines.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52193 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.