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Studies on the Metal–Amide Bond.
V*. The Crystal structure of Aqua[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane]copper(II) Monohydrate

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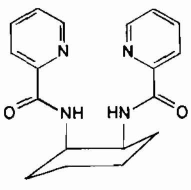
*Aqua[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane]copper(II) monohydrate, $C_{18}H_{22}N_4O_4$-Cu, is monoclinic, space group C2/c, with* a = *19.239(9),* b = *12.136(4),* c = *16.351(6) Å, β = 108.5(1)°, Z = 8. The structure was refined to* R = *0.085 for 1812 photographic reflexions using full-matrix least-squares calculations. The copper atom is five-coordinate with the N_4-tetradentate ligand encompassing the base of a distorted square-based pyramid [average Cu–N(*amide*) 1.928(8), Cu–N (*pyridine*) 2.044(8) Å, N(*amide*)–Cu–N(*amide*) 83.5(3)° N(*pyridine*)–Cu–N(*pyridine*) 110.4(3)°] and with the Cu atom displaced 0.21 Å above the N_4-plane towards the apical water molecule (Cu–O 2.303(8) Å). Both amide nitrogen atoms show significant pyramidal distortions. The cyclohexane ring adopts a 'skew-chair' conformation with the two methine hydrogens in a* trans-*configuration. The molecules pack in the lattice in layers parallel to (10$\bar{1}$) and a hydrogen-bond network involving both water molecules and the amide oxygen atoms of the ligand is evident.*

Introduction

Several examples of deprotonated bis-amides with the picolinamide unit as a basic component have been shown to act as tetradentate N_4 ligands [1, 2]. As part of a systematic study on the metal-amide bond the ligand N,N′-bis(2′-pyridinecarboxamide)-1,2-cyclohexane, bpchH_2 (I), has been synthesised and its coordination to some transition-metals has been reported [3]. Since the ligand was derived from a mixture of *cis*- and *trans*-1,2-diaminocyclohexane then complexes of both isomeric forms are feasible. Three forms of the deprotonated copper complex were observed to co-crystallise, having been identified by preliminary X-ray studies. We report here the crystal structure of one of these forms, namely, aqua-[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane]copper(II) monohydrate, [Cu(*trans*-bpch)-H_2O]H_2O.



(I)

Experimental

A hot ethanolic solution of bpchH_2 was added to a hot aqueous solution of copper acetate; violet-blue crystals formed on cooling. The crystals are diamond-shaped plates elongated along [001] and lying on (100).

Crystal Data

$C_{18}H_{22}N_4O_4Cu$, M_r = 421.9, Monoclinic, a = 19.239(9), b = 12.136(4), c = 16.351(6) Å, β = 108.5(1)°, U = 3620.0 Å^3, Z = 8, D_c = 1.548 Mgm^{-3}, $F(000)$ = 1752, $\mu(\text{Cu-}K_\alpha)$ = 2.25 mm^{-1} $\mu(\text{Mo-}K_\alpha)$ = 1.34 mm^{-1}. Systematic absences: hkl if $h + k \neq 2n$, and $h0l$ if $l \neq 2n$, space group Cc (No. 9) or $C2/c$ (No. 15).

Cell parameters were determined from precession photographs using Mo-K_α radiation. 2350 non-zero reflexions were recorded on layers $h0$–$6l$ from equi-inclination Weissenberg photographs using Cu-K_α radiation and on layers 0–$3kl$ and $hk0$–3 from precession photographs using Mo-K_α radiation. Intensities were estimated visually and corrected for Lorentz and polarization effects but not for extinction or absorption. The observed structure factors were placed on a common scale by internal correlation generating a unique data set of 1812 reflexions. Scattering factor curves were taken from International Tables for X-Ray Crystallography [4]. All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S.

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*Part IV is Reference [3].

TABLE I. Final Atomic Coordinates (fractional $\times 10^4$) with Estimated Standard Deviations in Parentheses.

	x	y	z
Cu	2136.3(6)	790.4(11)	1121.0(8)
O(W1)	1557(4)	1026(7)	2143(5)
O(1)	630(4)	1666(6)	−1148(4)
O(2)	2789(5)	−2323(7)	1716(6)
N(11)	1996(4)	2426(6)	814(4)
N(21)	3127(4)	535(8)	2042(5)
N(1)	1335(4)	658(7)	58(5)
N(2)	2168(4)	−792(7)	1037(5)
C(1)	1156(6)	−495(9)	−245(8)
C(2)	1494(6)	−1250(10)	433(6)
C(3)	1458(7)	−2449(11)	212(11)
C(4)	735(8)	−2745(11)	−427(10)
C(5)	349(8)	−1972(12)	−1114(10)
C(6)	430(6)	−742(11)	−828(7)
C(11)	1474(5)	2572(9)	55(6)
C(12)	1301(5)	3592(10)	−309(7)
C(13)	1683(6)	4520(9)	137(7)
C(14)	2213(5)	4382(9)	914(6)
C(15)	2359(5)	3317(10)	1241(6)
C(21)	3286(5)	−519(10)	2130(6)
C(22)	3942(6)	−943(11)	2714(8)
C(23)	4427(6)	−168(12)	3190(8)
C(24)	4268(6)	968(13)	3118(8)
C(25)	3609(5)	1281(10)	2520(7)
C(01)	1100(5)	1562(9)	−418(6)
C(02)	2721(5)	−1310(10)	1592(6)
O(W2)	869(4)	−1006(7)	2352(5)

TABLE III. Hydrogen Atom Parameters (coordinates: fractional $\times 10^3$).[a]

	x	y	z
H(1)	148	−43	−62
H(2)	118	−123	80
H(31)	118	−25	−10
H(32)	116	−296	74
H(41)	42	−315	−12
H(42)	83	−336	−78
H(51)	45	−216	−166
H(52)	−17	−211	−116
H(61)	37	−25	−133
H(62)	8	−52	−52
H(12)	91	367	−88
H(13)	157	528	−11
H(14)	249	503	123
H(15)	274	321	182
H(22)	405	−176	278
H(23)	491	−41	360
H(24)	461	152	349
H(25)	348	209	244
H(W11)	175	159	251
H(W12)	132	37	220
H(W21)	45	−129	197
H(W22)	78	−128	283

[a] For all H atoms $B = 6.0$ Å^2.

TABLE II. Final Anisotropic Thermal Parameters ($\times 10^4$) in the form $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$, with Estimated Standard Deviations in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	25.8(4)	46.2(10)	41.0(6)	0.5(6)	5.0(6)	0.4(7)
O(W1)	48(3)	89(8)	52(4)	−18(4)	20(3)	−16(4)
O(1)	33(2)	82(7)	39(3)	11(3)	−4(2)	6(4)
O(2)	55(4)	66(8)	71(5)	3(5)	−7(3)	5(5)
N(11)	19(2)	46(6)	30(3)	−2(3)	0(2)	−3(4)
N(21)	19(2)	67(9)	40(3)	6(4)	3(2)	2(5)
N(1)	23(2)	57(8)	40(3)	−4(4)	9(2)	−5(5)
N(2)	26(2)	55(7)	41(3)	4(4)	7(2)	4(5)
C(1)	33(3)	50(9)	60(6)	16(5)	−3(4)	12(6)
C(2)	44(4)	69(10)	38(5)	14(6)	6(4)	8(6)
C(3)	43(5)	75(12)	103(10)	26(7)	−2(6)	−7(9)
C(4)	51(5)	62(11)	90(9)	−13(7)	−13(6)	−9(8)
C(5)	48(5)	72(12)	97(9)	15(7)	−6(6)	−28(9)
C(6)	35(4)	85(11)	52(5)	−14(6)	1(4)	1(7)
C(11)	23(3)	65(9)	32(4)	6(4)	8(3)	−7(5)
C(12)	22(3)	70(10)	54(5)	1(5)	3(3)	19(7)
C(13)	36(4)	39(8)	56(6)	−3(5)	13(4)	13(6)
C(14)	33(3)	47(9)	40(4)	−4(5)	15(3)	−2(5)
C(15)	28(3)	88(11)	37(4)	−14(5)	11(3)	−3(6)
C(21)	25(3)	62(10)	38(4)	9(4)	9(3)	4(5)

(continued on facing page)

TABLE II. *(continued)*

	b_{12}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(22)	29(3)	91(12)	57(6)	15(5)	1(4)	4(7)
C(23)	36(4)	91(13)	68(7)	17(6)	1(5)	5(8)
C(24)	27(3)	126(17)	65(7)	−10(6)	−4(4)	0(9)
C(25)	25(3)	68(10)	52(5)	0(5)	−10(3)	−10(6)
C(01)	19(2)	60(9)	34(4)	−1(4)	3(3)	−1(5)
C(O2)	31(3)	66(10)	32(4)	7(5)	10(3)	−3(6)
O(W2)	34(2)	96(8)	57(4)	4(4)	11(3)	7(5)

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

Distances (Å)

	Cu–O(W1)	2.303(8)
	n = 1	*n* = 2
Cu–N(*n*1)	2.044(8)	2.043(7)
Cu–N(*n*)	1.930(7)	1.927(9)
N(*n*1)–C(*n*5)	1.355(13)	1.353(13)
C(*n*5)–C(*n*4)	1.392(15)	1.387(14)
C(*n*4)–C(*n*3)	1.363(14)	1.408(18)
C(*n*3)–C(*n*2)	1.415(15)	1.378(17)
C(*n*2)–C(*n*1)	1.368(14)	1.416(13)
C(*n*1)–N(*n*1)	1.337(11)	1.312(12)
C(*n*1)–C(O*n*)	1.505(14)	1.506(15)
C(O*n*)–O(*n*)	1.255(10)	1.246(13)
C(O*n*)–N(*n*)	1.338(12)	1.317(12)
N(*n*)–C(*n*)	1.488(14)	1.468(13)

C(1)–C(2)	1.426(15)	C(5)–C(4)	1.470(20)
C(1)–C(6)	1.451(14)	C(2)–C(3)	1.495(17)
C(6)–C(5)	1.558(17)	C(3)–C(4)	1.495(18)

Angles (°)

N(1)–Cu–N(21)	160.6(3)	N(2)–Cu–N(11)	162.6(3)
N(1)–Cu–N(2)	83.5(3)	N(11)–Cu–N(21)	110.4(3)

	n = 1	*n* = 2
N(*n*)–Cu–N(*n*1)	81.6(3)	81.8(3)
N(*n*1)–Cu–O(W1)	90.1(3)	92.1(3)
N(*n*)–Cu–O(W1)	103.4(3)	102.1(3)
C(*n*5)–N(*n*1)–Cu	130.0(7)	129.2(7)
C(*n*1)–N(*n*1)–Cu	111.0(6)	111.0(6)
C(*n*5)–N(*n*1)–C(*n*1)	119.0(9)	119.8(8)
C(O*n*)–N(*n*)–Cu	118.8(7)	117.6(7)
C(*n*)–N(*n*)–Cu	114.4(6)	112.6(7)
C(*n*)–N(*n*)–C(O*n*)	125.3(8)	129.0(10)
C(*n*1)–C(O*n*)–N(*n*)	110.6(8)	111.9(10)
C(*n*1)–C(O*n*)–O(*n*)	119.3(9)	121.0(10)
O(*n*)–C(O*n*)–N(*n*)	130.1(9)	127.1(9)
C(*n*2)–C(*n*1)–N(*n*1)	122.1(10)	123.7(10)
C(*n*2)–C(*n*1)–C(O*n*)	120.2(9)	119.1(8)
N(*n*1)–C(*n*1)–C(O*n*)	117.6(9)	117.2(11)
C(*n*3)–C(*n*2)–C(*n*1)	118.8(9)	115.6(12)
C(*n*4)–C(*n*3)–C(*n*2)	119.7(10)	122.1(11)
C(*n*5)–C(*n*4)–C(*n*3)	118.1(9)	116.9(11)
N(*n*1)–C(*n*5)–C(*n*4)	122.3(9)	122.0(11)

TABLE IV. *(continued)*

N(1)–C(1)–C(2)	110.2(8)	N(2)–C(2)–C(1)	111.6(10)
N(1)–C(1)–C(6)	119.1(9)	N(2)–C(2)–C(3)	119.7(10)
C(6)–C(1)–C(2)	119.0(10)	C(3)–C(2)–C(1)	117.6(11)
C(2)–C(3)–C(4)	111.4(10)	C(1)–C(6)–C(5)	112.2(10)
C(3)–C(4)–C(5)	120.9(12)	C(6)–C(5)–C(4)	113.8(12)

Structure Determination

A three dimensional Patterson synthesis indicated the space group to be centric and this was confirmed by successful analysis. The structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations in which the function minimized was $\Sigma w\Delta^2$. Initially a weight, w, of unity was given for each reflexion, and in the final cycles $w = (2.0 + 0.04|F_o| + 0.0001|F_o|^2)^{-1}$ was used. After isotropic refinement a difference map was calculated which gave the approximate positions of the hydrogen atoms. The positions of these atoms were optimised assuming C–H and O–H to be 1.0 and 0.9 Å respectively. They were included in subsequent calculations with thermal parameters of B = 6.0 Å^2 but their parameters were not refined. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms and was terminated when the maximum shift in any parameter was $<0.2\sigma$. The final value for R, based on 1812 reflexions, was 0.085 and for R' [$=(\Sigma w\Delta^2/\Sigma|F_o|^2)^{1/2}$] was 0.105. A final difference map showed no electron density $>|0.7|$ eÅ^{-3}. The final atomic parameters are given in Tables I–III. A list of structure factors has been deposited with the Editor.

Discussion

Bond lengths and angles in the molecule are listed in Table IV. A perspective drawing of the molecule is given in Fig. 1 with the atom labelling, and Fig. 2 shows the molecular packing in the unit cell [5].

TABLE V. Least-squares Planes Data.

(a) Least-square planes and their equations given by $lX' + mY' + nZ' - p = 0$, where X', Y' and Z' are orthogonal coordinates related to the atomic coordinates X, Y and Z by $X' = X \sin\beta$, $Y' = Y$ and $Z' = Z + X \cos\beta$. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	*m*	*n*	*p*
Plane (1): N(11), N(21), N(1), N(2) [N(11) –0.025; N(21) 0.025; N(1) 0.032; N(2) –0.032; Cu –0.21; O(W1) – 2.49]	0.5474	–0.0099	–0.8368	1.8954
Plane (2): N(11), C(11)–(15) [N(11) 0.004; C(11) –0.003; C(12), C(13) 0.001; C(14) > 0.001; C(15) –0.003; Cu 0.09; C(01) 0.05]	0.6851	–0.1067	–0.7206	2.0960
Plane (3): N(21), C(21)–(25) [N(21) –0.001; C(21) 0.001; C(22) –0.006;; C(23) 0.010; C(24) –0.009; C(25) 0.005; Cu 0.04; C(02) –0.03]	0.4377	0.0644	–0.8968	1.2576
Plane (4): N(11), C(11), C(01), N(1) [N(11) 0.012; C(11) –0.021; C(01) 0.020; N(1) –0.012; Cu 0.11; O(1) 0.05]	0.6990	–0.1079	–0.7069	2.1364
Plane (5): N(21), C(21), C(02), N(2) [N(21) –0.017; C(21) 0.030; C(02) –0.029; N(2) 0.016; Cu –0.07; O(2) 0.09]	0.4761	0.0390	–0.8785	1.5023
Plane (6): N(1), C(1), C(2), N(2) [N(1) –0.078; C(1) 0.143; C(2) –0.145; N(2) 0.080; Cu –0.22; C(01) 0.10; C(02) 0.27]	0.5927	–0.0748	–0.8019	2.0383
Plane (7): C(1), C(2), C(4), C(5) [C(1) 0.018; C(2) –0.019; C(4) 0.018; C(5) –0.018; C(3) 0.44; C(6) –0.48]	0.6900	–0.1835	–0.7002	2.3209
Plane (8): C(2), C(3), C(4)	0.3636	0.1955	–0.9108	0.8808
Plane (9): C(1), C(5), C(6)	0.3048	0.2287	–0.9245	1.5277
Plane (10): N(1), Cu, C(1) [C(01) 0.28]	0.6444	0.0600	–0.7623	2.1657
Plane (11): N(1), Cu, C(01) [C(1) 0.32]	0.6504	–0.1748	–0.7392	1.9762
Plane (12): N(1), C(1), C(01) [Cu 0.44]	0.8080	–0.0261	–0.5886	2.3702
Plane (13): N(2), Cu, C(2) [C(02) –0.18]	0.3908	0.0866	–0.9164	1.1212
Plane (14): N(2), Cu, C(02) [C(2) –0.21]	0.5299	0.0849	–0.8438	1.7004
Plane (15): N(2), C(2), C(02) [Cu –0.32]	0.4526	–0.0793	–0.8882	1.5356
Plane (16): C(01), C(11), O(1) [N(1) –0.03]	0.7167	–0.0909	–0.6914	2.2037
Plane (17): C(01), C(11), N(1) [O(1) –0.03]	0.7306	–0.1061	–0.6745	2.1798
Plane (18): C(01), O(1), N(1) [C(11) –0.04]	0.7119	–0.1232	–0.6914	2.1327
Plane (19): C(02), C(21), O(2) [N(2) –0.06]	0.5046	0.0619	–0.8611	1.7917

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TABLE V. *(continued)*

	l	*m*	*n*	*p*
Plane (20): C(02), C(21), N(2) [O(2) −0.05]	0.4794	−0.0261	−0.8771	1.5953
Plane (21): C(02), O(2), N(2) [C(21) −0.07]	0.4574	−0.0700	−0.8865	1.5466

(b) Dihedral angles (°) between relevant planes.

1–2	11.7	10–11	13.6	16–17	1.5	7–8	31.5
1–3	8.3	10–12	14.6	16–18	1.9	7–9	35.3
1–4	12.8	11–12	15.2	17–18	1.8	8–9	4.0
1–5	5.5	13–14	9.0	19–20	2.7		
2–3	20.1	13–15	10.3	19–21	3.1		
2–4	2.0	14–15	10.7	20–21	2.9		
3–5	2.9						
4–5	18.3						

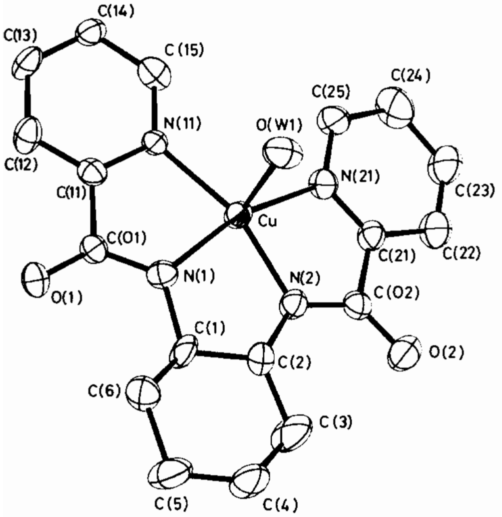

Fig. 1. A perspective drawing of the chelate molecule [5] and the labelling of the atoms. Thermal ellipsoids are drawn to include 35% probability.

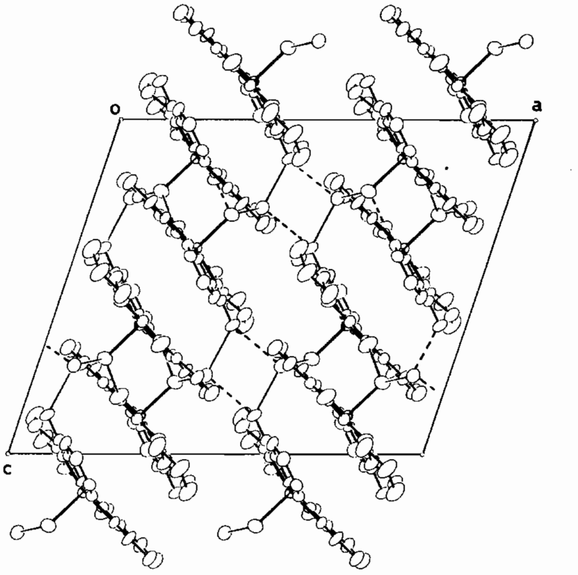

Fig. 2. The packing of the molecules showing the hydrogen-bonding network. The hydrogen bonds are represented by thin lines and broken lines, the latter indicating that one of the atoms involved is a *b*-cell translation away from that represented.

The copper atom is five-coordinate, the N_4-tetradentate ligand encompassing the base of a distorted square-based pyramid and a water molecule (Cu–O(W1) 2.303(8) Å) occupying the apical site. The copper atom is displaced by 0.21 Å above the basal square-plane, defined by the four nitrogen atoms (Table V, plane 1), towards the water molecule. The distortions from true square-planarity are due to the steric requirements of both the ligand and metal atom. Further distortion of the square-based pyramid is evidenced by the 'leaning' of the Cu–O(W1) bond by 8.7° from the normal to the N_4-plane towards the open side of the ligand. The average Cu–N(*amide*) distance is 1.928(8) Å which is shorter than the Cu–N(*pyridine*) distance of 2.044(8) Å, and is comparable with other deprotonated amide and peptide complexes [1, 2, 6]. The bond lengths and angles about the copper atom are similar to analogous deprotonated copper complexes in which the picolinamide group is a basic unit [1, 2].

Both of the amide five-membered chelate rings deviate slightly from planarity (Table V, planes 4 and 5), with the copper atom lying significantly out from each plane. The third five-membered chelate ring which contains the ethylene link is necessarily non-planar (Table V, plane 6). The two pyridine rings are planar (Table V, planes 2 and 3) and are each almost co-planar with their respective five-membered amide chelate rings. The dihedral angles between the N_4-plane and the pyridine ring planes are 11.7 and 8.3° respectively and that between the two ring planes is 20.1°. Such folding of the picolinamide moieties help to elevate the steric interaction of the pyridyl hydrogens in the 6-position but even so, the H(15)····H(25) contact distance of 2.00 Å is relatively close.

Both of the carbonyl carbon atoms have the expected trigonal-planar geometry (Table V, planes 16–21), but the two amide nitrogen atoms deviate significantly from planarity towards a pyramidal arrangement. The distortion, as measured by the average of the dihedral angles between the relevant three atom planes (Table V, planes 10–15), is 14.5° for N(1) and 10.0° for N(2). These values should be compared to those of 0 and 60° for trigonal-planar and pyramidal geometries respectively. These distortions with respect to the molecular plane are in opposite directions as determined by the conformation of the cyclohexane ring.

The cyclohexane ring adopts a skew-chair conformation, with the two methine hydrogens, H(1) and H(2), in a *trans* configuration. The two three atom planes are almost parallel (Table V, planes 8 and 9) and make an average angle of 33° with the 'seat' of the chair defined by the atoms C(1), C(2), C(4), C(5) (Table I, plane 7). This angle is considerably less than 54.7° for an ideal chair conformation. Since the complex crystallises in a centric space group both *R*,*R*- and *S*,*S*-enantiomers are present in the crystal.

Both water molecules are involved in hydrogen-bonding. The coordinated water molecule O(W1) is hydrogen-bonded to the lattice water molecule [O(W1)–H(W11)····O(W2) 2.87(1) Å] and to a carbonyl oxygen atom of a neighbouring molecule [O(W1)–H(W12)····O(2) at ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) 2.76(1) Å]. The lattice water molecule forms hydrogen-bonds to carbonyl oxygen atoms of two adjacent chelate molecules [O(W2)–H(W21)····O(1) at ($\bar{x}, \bar{y}, \bar{z}$) 3.04(1) Å; O(W2)–H(W22)····O(1) at ($x, \bar{y}, \frac{1}{2} + z$) 2.76(1) Å]. As a result of this hydrogen-bonding network the chelate molecules pack in layers parallel to ($10\bar{1}$). This packing arrangement is similar to that found in the analogous [Cu(bpen)-H_2O]H_2O structure [1] which contains a central ethylene link.

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