Bis[μ-N,N'-bis(quinolin-8-yl)pyridine-2,6-dicarboxamido]dizinc(II) dichloromethane disolvate

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The title compound, [Zn$_2$(C$_{25}$H$_{15}$N$_5$O$_2$)$_2$]·2CH$_2$Cl$_2$, is a dinuclear double-helical complex which lies on a crystallographic twofold axis. In the complex, both ligands are partitioned into two tridentate domains which allow each ligand to bridge both metal centres. Each Zn^{II} atom is six-coordinated in a distorted octahedral environment formed by two amide N atoms, two quinoline N atoms and two pyridine N atoms from two different ligand molecules, with the central pyridine ring, unusually, bridging two Zn^{II} atoms. The deprotonated ligand is not planar, the amide side chains being considerably twisted out from the plane of the central pyridine ring.

Comment

The design and construction of double- and triple-helical complexes has attracted intense interest, not only for their fascinating structural and superstructural diversity (Piguet *et al.*, 1997; Elsevier *et al.*, 2003), but also for their potential applications in medicinal chemistry (Richards & Rodger, 2007), nonlinear optics (Serrano & Sierra, 2003), asymmetric catalysis (Yeung *et al.*, 2008) and luminescence (Riis-Johannessen *et al.*, 2009). Since the early pioneering work of Lehn and co-workers on double-helical Cu^I complexes (Sleiman *et al.*, 1995), a wide range of multidentate ligands have been developed for the formation of helicates. Notable examples include the *O,O*-donor biscatecholates (Albrecht & Schneider, 2002), the all-*N*-donor mixed pyridine–thiazole ligands (Rice *et al.*, 2001), the *N,O*-donor pyrazole–phenol ligands (Ronson *et al.*, 2006) and the mixed *N,N/N,O*-donor pyridine–benzimidazole/amide ligands (Piguet *et al.*, 1997). Depending on the carefully designed ligands and the versatile coordination geometries of the chosen metal, a large number of polynuclear metal clusters with magnetic, optical or electronic properties have been synthesized. The synthesis of

ligands based on 2,6-disubstituted pyridine has attracted a great deal of attention. In particular, diamides incorporating an –NH–CO–pyridine–CO–NH– core are versatile ligands, and a number of novel architectures such as helicates, cages, pockets and rotaxanes have recently been prepared (Lincheneau *et al.*, 2010; Pan *et al.*, 2010; Miyagawa *et al.*, 2010). However, no dinuclear double-helical complex based on N,N'-bis(quinolin-8-yl)pyridine-2,6-dicarboxamide (H$_2$L) has been reported to date. In this paper, we describe the synthesis of the title novel dinuclear Zn^{II} double helicate, [Zn$_2$L$_2$]·2CH$_2$Cl$_2$, (I), by the reaction of H$_2$L with Zn(OAc)$_2$·2H$_2$O. The compound has been characterized by elemental analysis, ^{1}H and ^{13}C{H} NMR and IR spectroscopies, and X-ray single-crystal analysis.

(I)
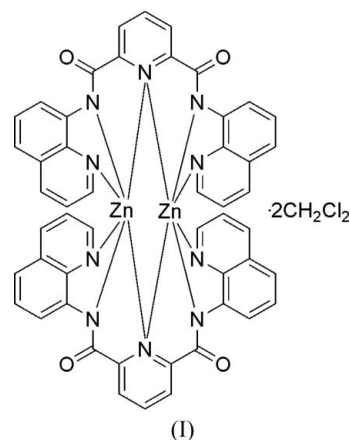
The molecular structure of (I) is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 1. Complex (I) is a dinuclear double helicate and there is only
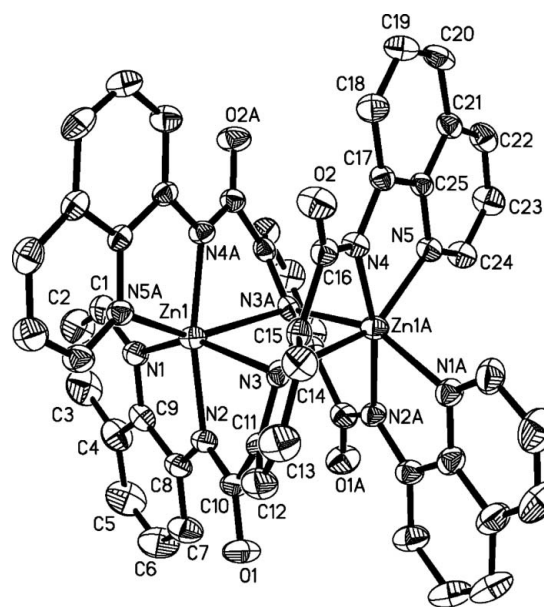

Figure 1
The Zn^{II} coordination environments in (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms and the solvent have been omitted for clarity. Atoms labelled with the suffix A and unlabelled atoms are at the symmetry position $(-x + 1, y, -z + \frac{1}{2})$.

metal-organic compounds

half a [Zn₂L₂] unit in the asymmetric unit, with the other half related to it by a crystallographic twofold axis. The Zn^{II} atom in the dimeric complex is coordinated to two amide N atoms [N2 and N4^i; symmetry code: (i) $-x + 1$, y, $-z + \frac{1}{2}$], two quinoline N atoms (N1 and N5^i) and two pyridine N atoms (N3 and N3^i) from two different ligand molecules. Each Zn^{II} atom has a distorted octahedral configuration, the r.m.s. deviation of the constituent atoms from the mean equatorial plane defined by atoms N1/N2/N3^i/N4^i being 0.0383 (6) Å. The axial positions at Zn1 are occupied by atoms N3 and N5^i, and atom Zn1 deviates from the equatorial plane by 0.1485 (13) Å towards axial atom N5^i. Thus, the dimer is made up of two octahedra which are joined at a common edge, with the two bridging pyridine N atoms forming slightly asymmetric bridges between the two Zn^{II} atoms. Most of the bond angles at Zn deviate considerably from the ideal values of 90 and 180°, as can be seen from Table 1. The Zn—N bond lengths are close to those reported for a dinuclear zinc(II) complex of 2,6-diacetylpyridine bis(2-pyridylhydrazone) (Wester & Palenik, 1976). Due to the bridging nature of the pyridine (py) N atoms, the Zn—N$_{py}$ distances are relatively long, with Zn1—N3 = 2.449 (3) Å and Zn1—N3^i = 2.560 (3) Å, while the remaining four Zn—N distances average 2.05 Å. As a consequence of the central bridging N$_{py}$ atoms in the [Zn(μ-N₂)Zn]$^{4+}$ core, the Zn1···Zn1^i separation within the binuclear unit is 3.445 (2) Å, which is short compared with other Zn^{II}-containing helicates (Horn *et al.*, 2003; Ronson *et al.*, 2005), and the Zn—N$_{py}$—Zn bridging angle is 86.91 (12)°.

Interestingly, in contrast with the previously reported free ligand H₂L (Meghdadi *et al.*, 2008), striking changes have taken place in the conformation of the anion *L*. In H₂L, the central pyridine ring is oriented at dihedral angles of 8.90 (4) and 28.67 (4)° with respect to the two planar quinolyl ring systems, and the quinolyl systems themselves are oriented at a dihedral angle of 24.68 (3)° (Meghdadi *et al.*, 2008), while in complex (I), the amide side chains are definitely twisted out of the plane of the central pyridine ring by considerable amounts. The dihedal angles between the central pyridine ring and the two quinolyl systems of (I) are 38.61 (16) and 41.72 (16)°, and the quinolyl systems are inclined at 69.63 (11)° with respect to each other. The lack of planarity of the amide is obviously related to its coordinating behaviour.

Experimental

To a solution of pyridine-2,6-dicarboxylic acid (1.67 g, 0.01 mmol) in pyridine (5 ml) was added 8-aminoquinoline (2.88 g, 0.02 mmol) and the resulting solution warmed with stirring for 30 min. Triphenyl phosphite (6.2 g, 0.02 mmol) was added slowly and the mixture was stirred at 393 K for 10 h. On cooling to room temperature, the white precipitate which had formed was filtered off and recrystallized from chloroform to afford H₂L (yield 7.02 g, 16.75 mmol, 84%; m.p. 561–562 K). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.18 (*s*, 2H), 8.92 (*dd*, 2H), 8.57–8.54 (*m*, 2H), 8.50–8.42 (*m*, 3H), 8.26 (*dd*, 2H), 7.84–7.81 (*m*, 2H), 7.76–7.71 (*m*, 2H), 7.55 (*q*, 2H); IR (KBr, ν, cm^{-1}): 3322, 3298, 1684, 1544, 1490, 1428, 1328, 1149, 1068, 1000, 890, 826, 794, 751, 709, 679, 604. Elemental analysis calculated for C₅₀H₁₇N₅O₂: C 71.59, H 4.09, N 16.70%; found: C 71.33, H 4.06, N 16.53%.

A mixture of H₂L (0.3355 g, 0.80 mmol) and Zn(OAc)₂·2H₂O (0.1758 g, 0.80 mmol) in ethanol (20 ml) was refluxed for 6 h. The resulting precipitate was filtered off, washed with chloroform and then ethanol, and finally dried in air. Recrystallization from CH₂Cl₂ yielded yellow crystals of (I) suitable for X-ray diffraction upon slow evaporation. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.87 (*d*, 4H), 8.35 (*d*, 4H), 7.71 (*d*, 4H), 7.62 (*t*, 4H), 7.52 (*d*, 4H), 7.36–7.33 (*m*, 2H), 7.28–7.23 (*m*, 8H); ^{13}C{H} NMR (500 MHz, DMSO-d_6): δ 202.1, 165.9, 155.4, 145.7, 142.1, 139.6, 139.4, 129.0, 128.4, 123.1, 121.5, 120.9, 119.4; IR (KBr, ν, cm^{-1}): 3425, 1612, 1581, 1500, 1463, 1413, 1390, 1350, 1317, 1271, 1238, 1158, 1082, 965, 829, 758, 609. Elemental analysis calculated for C₅₀H₃₀N₁₀O₄Zn₂: C 62.19, H 3.13, N 14.50%; found: C 61.94, H 3.09, N 14.32%.

Crystal data

[Zn₂(C₂₅H₁₅N₅O₂)₂]·2CH₂Cl₂	$V = 4894$ (2) Å^3
$M_r = 1135.43$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 24.458$ (5) Å	$\mu = 1.26$ mm^{-1}
$b = 13.672$ (3) Å	$T = 293$ K
$c = 16.588$ (3) Å	$0.40 \times 0.30 \times 0.20$ mm
$\beta = 118.07$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	4445 independent reflections
Absorption correction: ψ scan (*CAD-4 EXPRESS*; Enraf–Nonius, 1994)	2882 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.023$
	3 standard reflections every 200 reflections
$T_{min} = 0.642$, $T_{max} = 0.778$	intensity decay: 1%
4554 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	36 restraints
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
4445 reflections	$\Delta\rho_{min} = -0.72$ e Å^{-3}
354 parameters	

Table 1
Selected geometric parameters (Å, °).

Zn1—N2	1.987 (3)	Zn1—N1	2.134 (4)
Zn1—N4^i	2.003 (3)	Zn1—N3	2.449 (3)
Zn1—N5^i	2.097 (3)	Zn1—N3^i	2.560 (3)
N2—Zn1—N4^i	166.94 (13)	N5^i—Zn1—N3	84.59 (12)
N2—Zn1—N5^i	111.37 (14)	N1—Zn1—N3	154.75 (13)
N4^i—Zn1—N5^i	80.88 (13)	N2—Zn1—N3^i	94.10 (13)
N2—Zn1—N1	79.79 (14)	N4^i—Zn1—N3^i	73.09 (12)
N4^i—Zn1—N1	100.94 (13)	N5^i—Zn1—N3^i	152.66 (12)
N5^i—Zn1—N1	109.06 (14)	N1—Zn1—N3^i	84.39 (12)
N2—Zn1—N3	75.39 (13)	N3—Zn1—N3^i	92.74 (11)
N4^i—Zn1—N3	102.19 (13)		

Symmetry code: (i) $-x + 1$, y, $-z + \frac{1}{2}$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 (aromatic) and 0.97 Å (solvent), and with U_{iso}(H) = 1.2U_{eq}(C). The CH₂Cl₂ solvent molecule is disordered and two overlapping orientations of the molecule were defined with their site-occupation factors constrained to sum to 1.0. The atomic displacement parameters of the Cl atoms were restrained to be similar with a tolerance of 0.04 Å^2. The site-occupation factor of the major orientation, which contains atom C26′, refined to 0.58 (2).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3146). Services for accessing these data are described at the back of the journal.

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