# 1,3-Bis(2,2':6',2''-terpyridin-4'-yl)benzene, a new dinucleating bis(tridentate) ligand, as its dichloromethane solvate

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The title compound, 1,3-bis(2,2':6',2''-terpyridin-4'-yl)benzene dichloromethane solvate, $C_{36}H_{24}N_6 \cdot CH_2Cl_2$, is a new ligand suitable for bridging two metal centres. Though not in binding conformations, its two terpyridine units are linked in a unique arrangement, through a *meta*-phenylene core, which disallows resonance communication between binding sites, as reflected by the crystal structure of its 1:1 $CH_2Cl_2$ solvate. The two terpyridine units are related by crystallographically imposed twofold symmetry, forming a 30.02 (8)° dihedral angle with the phenylene core, but with fairly coplanar pyridine rings within. The solvent molecule is disordered over the twofold axis.

## Comment

1,4-Bis(2,2':6',2''-terpyridin-4'-yl)benzene, the so-called 'back-to-back' bis(terpyridine), is known (Kröhnke, 1976; Constable & Cargill-Thompson, 1992; Vaduvescu & Potvin, 2002) and has been used as a bridging ligand in polynuclear complexes of Ru and other metals (Collin *et al.*, 1993; Barigelletti *et al.*, 1994; Janini *et al.*, 1999; Vaduvescu & Potvin, 2002), but has apparently not appeared in any crystal structure. The title compound, (I), is the *meta*-linked isomer, which has been prepared to study the electrochemical and spectroscopic properties of the analogous di- and trinuclear Ru complexes lacking a resonance route of communication between metal centres. The effect of this lack of resonance on the structure of the free ligand was, therefore, of interest.



(I)
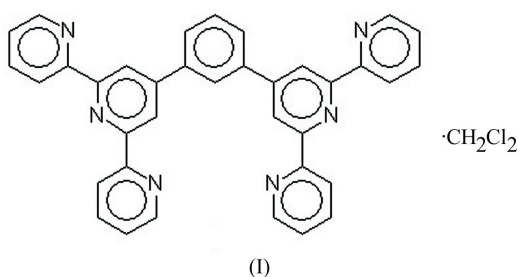
The ligand was easily prepared by a one-pot synthesis from isophthalaldehyde, 2-acetylpyridine and $NH_4OAc$, a remarkable reaction in which seven molecules condense at once. The yield (37%) is comparable to yields obtained for the *para*-phenylene-linked isomer.

It co-crystallized with $CH_2Cl_2$ in the space group *Pccn*. The ligand molecule (Fig. 1) resides on a twofold axis, which runs through atoms C1 and C4 of the central phenylene ring. The solvent molecule is disordered over a twofold axis. The terpyridine units are in a non-chelating conformation to avoid electron-pair repulsions. The three pyridine moieties in each unit are fairly coplanar [interplanar dihedral angles 8.81 (15) and 8.04 (16)°], but the phenylene linker is twisted 30.02 (8)°
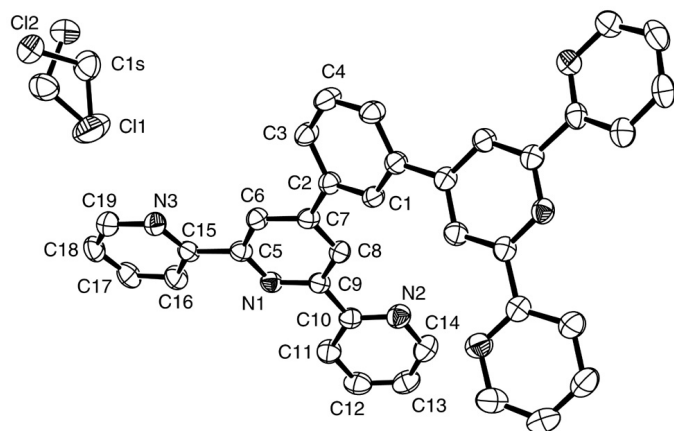
**Figure 1**
A view of (I), showing the atomic numbering scheme, with H atoms omitted, and displacement ellipsoids drawn at the 50% probability level.

out of coplanarity with each central pyridine. The bond lengths are as expected, with no significant difference among the three inter-ring bonds, which, along with the *ca* 30° twist, is consistent with a lack of significant π-communication.

## Experimental

2-Acetylpyridine (1.00 g, 8.3 mmol) was added to a solution of isophthalaldehyde (0.2764 g, 2.1 mmol) in $CH_3OH$ (100 ml). 15% Aqueous KOH (2.3 ml) and concentrated $NH_4OH$ (23 ml) were then added to the solution. Vigorous stirring was maintained at reflux for 2 d. The yellow precipitate that formed was isolated by vacuum filtration, washed with water to neutral pH and dissolved in $CHCl_3$ (40 ml). The resulting solution was washed with $H_2O$ (3 × 30 ml). The organic fraction was dried with $MgSO_4$ and the solvent removed *in vacuo*. The residue was recrystallized in $CHCl_3/Et_2O$, yielding 0.4109 g (37%), m.p. > 573 K. $\delta_H$ ($CDCl_3$) 8.84 (*s*, 4H), 8.77 (*d*, 4H, *J* = 5.3 Hz), 8.73 (*d*, 4H, *J* = 8.1 Hz), 8.35 (*s*, 1H), 8.01 (*d*, 2H, *J* = 7.9 Hz), 7.91 (*dd*, 4H, *J* = 8.1 Hz), 7.69 (*t*, 1H, *J* = 7.8 Hz), 7.38 (*dd*, 4H, *J* = 5.3 Hz) p.p.m. EI–MS *m/z* 540 (100); $C_{36}H_{24}N_6$ requires 540.6. Analysis found: C 79.25, H 4.63, N 14.93%; $C_{36}H_{24}N_6$ requires: C 79.98, H 4.47, N 15.54%. Colourless plate-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of a solution in $CH_2Cl_2$.

### Crystal data

| | |
|---|---|
| $C_{36}H_{24}N_6$·$CH_2Cl_2$ | Mo $K\alpha$ radiation |
| $M_r = 625.54$ | Cell parameters from 3806 |
| Orthorhombic, $Pccn$ | reflections |
| $a = 8.0259$ (16) Å | $\theta = 2.6$–27.5° |
| $b = 18.111$ (4) Å | $\mu = 0.26$ mm$^{-1}$ |
| $c = 20.590$ (4) Å | $T = 150$ (1) K |
| $V = 2992.8$ (10) Å$^3$ | Plate, colourless |
| $Z = 4$ | 0.30 × 0.20 × 0.08 mm |
| $D_x = 1.388$ Mg m$^{-3}$ | |

### Data collection

| | |
|---|---|
| Nonius KappaCCD diffractometer | $R_{int} = 0.107$ |
| $\varphi$ scans and $\omega$ scans with $\kappa$ offsets | $\theta_{max} = 25.0°$ |
| 21 389 measured reflections | $h = -9 \rightarrow 9$ |
| 2639 independent reflections | $k = -21 \rightarrow 21$ |
| 1822 reflections with $I > 2\sigma(I)$ | $l = -24 \rightarrow 24$ |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0822P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.063$ | $+ 1.8351P]$ |
| $wR(F^2) = 0.175$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.06$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2639 reflections | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |
| 215 parameters | $\Delta\rho_{min} = -0.51$ e Å$^{-3}$ |
| H-atom parameters constrained | Extinction correction: *SHELXTL* |
| | Extinction coefficient: 0.0055 (13) |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C5 | 1.336 (4) | N3—C19 | 1.346 (4) |
| N1—C9 | 1.344 (4) | C2—C7 | 1.486 (4) |
| N2—C10 | 1.335 (4) | C5—C15 | 1.492 (4) |
| N2—C14 | 1.351 (4) | C9—C10 | 1.486 (4) |
| N3—C15 | 1.343 (4) | | |
| C5—N1—C9 | 118.1 (2) | C8—C7—C2 | 121.0 (3) |
| C10—N2—C14 | 117.1 (3) | N1—C9—C10 | 116.7 (3) |
| C15—N3—C19 | 116.9 (3) | C8—C9—C10 | 121.0 (3) |
| C1—C2—C7 | 121.2 (2) | N2—C10—C11 | 122.6 (3) |
| C3—C2—C7 | 120.7 (3) | N2—C10—C9 | 117.1 (3) |
| N1—C5—C15 | 115.7 (2) | N3—C15—C5 | 116.9 (2) |
| C6—C5—C15 | 121.3 (2) | C16—C15—C5 | 120.5 (3) |
| C6—C7—C2 | 121.7 (2) | | |
| C3—C2—C7—C6 | −30.3 (4) | C6—C5—C15—C16 | 171.1 (3) |
| C8—C9—C10—C11 | 171.8 (3) | | |

The solvent molecule is disordered over a twofold axis. All H atoms were assigned calculated positions [C—H = 0.95 and 0.99 Å in the ligand molecule and solvent, respectively] and included in the refinement in riding-motion approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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