Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A sterically constrained bis(2,2′:6′,2″-terpyridine) ligand

Andrew C. Benniston, William Clegg,* Ross W. Harrington and Peiyi Li

School of Natural Sciences (Chemistry),
University of Newcastle upon Tyne,
Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail: w.clegg@ncl.ac.uk

Received 22 November 2004
Accepted 23 November 2004
Online 27 November 2004

Key indicators

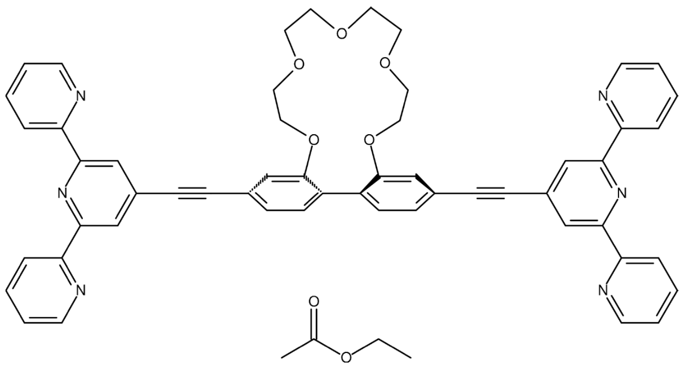
Single-crystal synchrotron study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.051
wR factor = 0.138
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, 4,4′-bis[(2,2′:6′,2″-terpyridin-4-yl)ethynyl]-2,2′-(3,6,9-trioxaundecane-1,11-diyldioxy)-1,1′-biphenyl-ethyl acetate solvate, $C_{54}H_{42}N_6O_5{\cdot}C_4H_8O_2$, is a sterically constrained ligand based on the well-known chelator 2,2′:6′,2″-terpyridine (terpy). Two terpy units are linked by ethynyl bridges to a central 2,2′-biphenyl unit, in which the two rings are connected by a polyether strand. The torsion angle between the two rings of the biphenyl unit is 113.25 (17)°. The crown ether ring is flexible and capable of complexing metal cations, and the two terpy units may be reorganized from their observed *trans-trans* configuration to act as terdentate ligands for transition metal ions.

Comment

Crystal structures have been reported of the terdentate ligand 2,2′:6′,2″-terpyridine (terpy) and its complexes (Constable, 1986); the Cambridge Structural Database (Version 5.25; Allen, 2002) contains 13 entries with uncomplexed and unsubstituted terpy and over 600 of its metal complexes. Linking together two terpy ligands *via* a bridging unit leads to the possibility of producing dinuclear and bimetallic complexes (Sauvage *et al.*, 1994). When the bridge is or contains a 2,2′-biphenyl unit, there exists the opportunity to control the torsion angle between the two rings if they are further connected (Lindsten *et al.*, 1987). The title compound, (I), represents such a constrained derivative, in which the two benzene rings of biphenyl are coupled *via* a pentaoxa cyclic polyether linker, itself capable of acting as a multidentate ligand to provide a third coordination site. In order to find the torsion angle of the biphenyl unit, crystals were grown and the molecular structure obtained crystallographically.



(I)

The molecular structure of (I), as an ethyl acetate solvate, is illustrated in Fig. 1. The N atoms of the terpy segments adopt the sterically preferred *trans–trans* arrangement generally

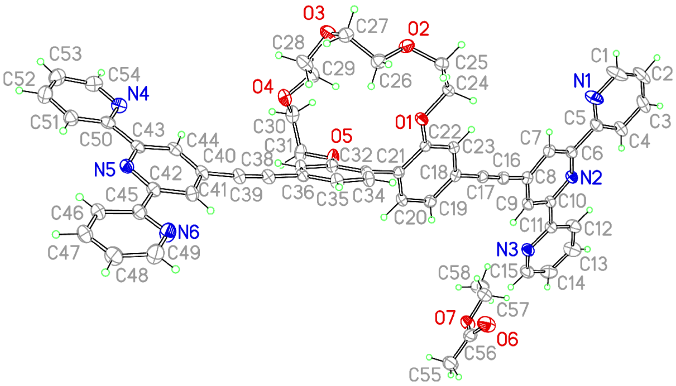


Figure 1
The molecular structure of the asymmetric unit of (I), showing atom labels and 50% probability ellipsoids for non-H atoms. Unlabelled atoms C32 and C37 are obscured by other atoms.

found when terpy is uncoordinated. The length of the C—C bond joining the benzene rings of the biphenyl unit is 1.490 (2) Å, similar to that found in 2,2′-biphenol monohydrate [1.491 (3) Å; Chen *et al.*, 1996]. The spanning polyether chain is sufficiently long and flexible to allow the biphenyl unit to adopt a twisted configuration with almost perpendicular rings. The torsion angle C22—C21—C33—C32 is 113.25 (17)°. There is only one previously reported example of a biphenyl unit with rings linked by such a pentaoxa polyether strand in this way (Costero *et al.*, 1996); it has two polyether strands, one of them uncomplexed and the other binding a mercury(II) ion, thus demonstrating the capability of this crown ether ring to serve as a ligand. The two polyether strands have very different conformations: the complexed one is *gauche* for all O—C—C—O linkages and *anti* for each C—O—C—C segment, in order to bring the O atoms into an essentially coplanar arrangement for coordination, but the uncomplexed one has a wide range of torsion angles, not all of which approximate to *gauche* or *anti*. A similarly unsystematic sequence of torsion angles is found in the title compound (Table 1), reflecting the flexibility of the uncomplexed polyether strand. The torsion angle for the biphenyl unit is similar in the two compounds (110.4° for the mercury complex).

All bond lengths and angles are normal. The skeleton of the molecule, comprising the central rings of the terpy units, the ethynyl bridges and the biphenyl unit, is close to linear, with little bending induced by steric or crystal packing interactions. There are no significant intermolecular interactions, and it is surprising that the ethyl acetate is retained in the crystal structure during recrystallization from a different solvent.

Experimental

The title compound was synthesized by a literature procedure (Benniston *et al.*, 2003). ^{1}H NMR spectroscopy indicated that it was an ethyl acetate solvate. Crystals suitable for X-ray diffraction were grown by slow vapour diffusion of diethyl ether into a chloroform solution; the ethyl acetate is retained in the crystal structure during this process.

Crystal data

$C_{54}H_{42}N_6O_5{\cdot}C_4H_8O_2$
$M_r = 943.04$
Monoclinic, $P2_1/c$
$a = 8.5942$ (12) Å
$b = 42.288$ (6) Å
$c = 13.8795$ (19) Å
$\beta = 101.839$ (3)°
$V = 4936.9$ (12) Å^3
$Z = 4$
$D_x = 1.269$ Mg m^{-3}

Synchrotron radiation
$\lambda = 0.6948$ Å
Cell parameters from 10 431 reflections
$\theta = 2.5$–29.2°
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.10 × 0.05 × 0.02 mm

Data collection

Bruker SMART 1K CCD diffractometer
Thin-slice ω scans
Absorption correction: none
18651 measured reflections
8957 independent reflections

7604 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -50 \rightarrow 45$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.138$
$S = 1.02$
8957 reflections
642 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.7718P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.34$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C5—C6—N2	172.56 (16)	C30—O4—C29—C28	−169.44 (15)
N2—C10—C11—N3	−174.29 (15)	O3—C28—C29—O4	−168.47 (15)
C24—O1—C22—C21	−176.50 (13)	C29—O4—C30—C31	107.96 (17)
C33—C21—C22—O1	1.5 (2)	C32—O5—C31—C30	94.08 (18)
C22—O1—C24—C25	−174.97 (13)	O4—C30—C31—O5	−64.32 (18)
C26—O2—C25—C24	101.55 (16)	C31—O5—C32—C33	179.55 (14)
O1—C24—C25—O2	−62.82 (17)	O5—C32—C33—C21	−4.4 (2)
C25—O2—C26—C27	168.42 (14)	C20—C21—C33—C34	109.81 (18)
C28—O3—C27—C26	79.72 (19)	C22—C21—C33—C32	113.25 (17)
O2—C26—C27—O3	66.46 (18)	N5—C42—C45—N6	−172.13 (15)
C27—O3—C28—C29	−136.94 (17)	N5—C43—C50—N4	−177.06 (13)

H atoms were positioned geometrically, with C—H = 0.95–0.99 Å, and refined with a riding model (including free rotation about C—C bonds), with $U_{\rm iso} = 1.2U_{\rm eq}$(C) ($1.5U_{\rm eq}$ for methyl groups).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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* and local programs.

We thank the EPSRC for financial support, including the national X-ray crystallography service synchrotron component, and the CCLRC for SRS beamtime allocation and financial support.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Benniston, A. C., Li, P. & Sams, C. A. (2003). *Tetrahedron Lett.* **44**, 3947–3949.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, X.-M., Luo, G.-B., Tong, M.-L. & Zhou, Z.-Y. (1996). *Acta Cryst.* C**52**, 1727–1729.

Andrew C. Benniston *et al.* • $C_{54}H_{42}N_6O_5{\cdot}C_4H_8O_2$ **o2453**

Constable, E. C. (1986). *Adv. Inorg. Chem. Radiochem.* **30**, 69–121.
Costero, A. M., Andreu, C., Monrabal, E., Tortajada, A., Ochando, L. E. & Amigo, J. M. (1996). *Tetrahedron*, **52**, 12499–12508.
Lindsten, G., Wennerström, O. & Isaksson, R. (1987). *J. Org. Chem.* **52**, 547–554.
Sauvage, J.-P., Collin, J.-P., Chambron, J.-C., Guillerez, S., Coudret, C., Balzani, V., Barigelletti, F., De Cola, L. & Flamigni, L. (1994). *Chem. Rev.* **94**, 993–1019.
Sheldrick, G. M. (2001). *SHELXTL*. Version 5. Bruker AXS Inc., Madison, Wisconsin, USA.