

Dimethyl 2,2'-bipyridine-6,6'-dicarboxylate and bis(dimethyl 2,2'-bipyridine-6,6'-dicarboxylato- κ^2N,N')copper(I) tetrafluoroborate

Alexander J. Blake, Neil R. Champness,* Pamela V. Mason and Claire Wilson

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, England

Correspondence e-mail: neil.champness@nottingham.ac.uk

Received 21 March 2007

Accepted 26 April 2007

Online 31 May 2007

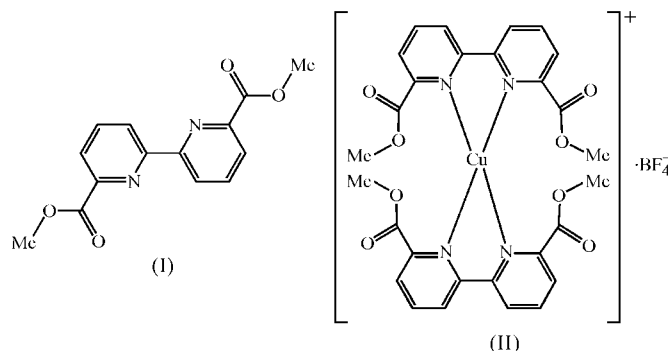
The single-crystal X-ray structures of dimethyl 2,2'-bipyridine-6,6'-dicarboxylate, $C_{14}H_{12}N_2O_4$, and the copper(I) coordination complex bis(dimethyl 2,2'-bipyridine-6,6'-dicarboxylato- κ^2N,N')copper(I) tetrafluoroborate, $[Cu(C_{14}H_{12}N_2O_4)_2]BF_4$, are reported. The uncoordinated ligand crystallizes across an inversion centre and adopts the anticipated *anti* pyridyl arrangement with coplanar pyridyl rings. In contrast, upon coordination of copper(I), the ligand adopts an arrangement of pyridyl donors facilitating chelating metal coordination and an increased inter-pyridyl twisting within each ligand. The distortion of each ligand contrasts with comparable copper(I) complexes of unfunctionalized 2,2'-bipyridine.

Comment

As part of our ongoing studies of multi-modal ligands for the construction of coordination polymers (Oxtoby *et al.*, 2002, 2003, 2005; Thébault *et al.*, 2006), we have prepared a diester-substituted 2,2'-bipyridyl ligand and a copper(I) complex that serve as potentially useful building blocks for subsequent synthetic procedures.

The diester-substituted 2,2'-bipyridyl molecule, dimethyl 2,2'-bipyridine-6,6'-dicarboxylate, (I), was synthesized by a HCl-catalyzed esterification method in MeOH. Single-crystal X-ray diffraction confirmed the identity of the product and demonstrated the lower energy conformation commonly adopted by uncoordinated 2,2'-bipyridyl systems, which has the pyridyl N atoms adopting an *anti* arrangement to avoid repulsive interactions between the nitrogen lone pairs. The entire molecule is almost planar in the solid state. An inversion centre between atoms C2 and C2¹ [symmetry code: (i) $-x, 1 - y, 1 - z$] ensures coplanarity of the two pyridyl rings, with the two ester groups exhibiting a slight deviation from the plane formed by the bipyridyl unit, with an N1—C6—C7—O8 torsion angle of 9.84 (16) $^\circ$ (Fig. 1).

Compound (I) was complexed to copper(I) in a 2:1 ligand-to-metal ratio *via* reaction of $[Cu(MeCN)_4]BF_4$ with the ligand in MeCN—CH₂Cl₂, to give bis(dimethyl 2,2'-bipyridine-6,6'-dicarboxylato)copper(I) tetrafluoroborate, (II). The crystal structure of (II) (Fig. 2) confirms the anticipated coordination environment in which the metal centre is coordinated solely by the bipyridyl units, with the ester groups not participating in metal coordination.



In the structure of (II), there are two short Cu—N bonds of 2.029 (3) and 2.035 (3) Å for Cu—N1 and Cu—N7', respectively, and two slightly longer bonds of 2.074 (3) and 2.077 (3) Å for Cu—N7 and Cu—N1', respectively. Three of the ester carbonyl O atoms point towards the Cu^I centre but no significant interactions are present; the Cu···O distances are longer than 2.9 Å, the combined sum of the van der Waals radii (Bondi, 1964).

This copper(I) complex adopts a distorted tetrahedral geometry, with an angle of 70 $^\circ$ between the planes defined by the two bipyridyl units. This distortion is only slightly greater than the comparable angles observed in bis(2,2'-bipyridine)-copper(I) perchlorate (76 $^\circ$; Munakata *et al.*, 1987) and bis(2,2'-bipyridine)copper(I) trifluoromethanesulfonate (85 $^\circ$; Tomislav, 2006). Steric interactions between the bulkier dimethyl 2,2'-bipyridine-6,6'-dicarboxylate ligands may account for the slight increase in the distortion of the relatively malleable tetrahedral Cu^I coordination environment.

By comparison with the crystal structure of the free ligand, (I), it can be seen that the ligand in (II) adopts a different conformation on complexation, as anticipated, allowing chelation of the metal centre by the bipyridyl species. The

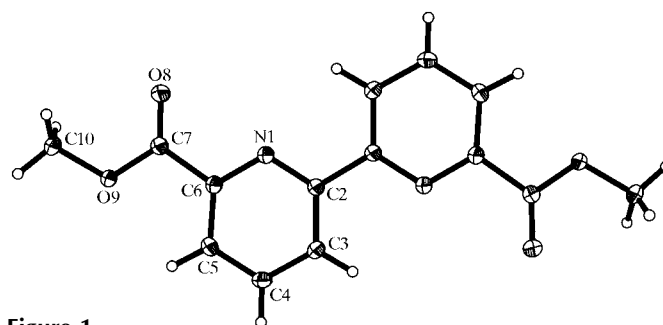


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator ($x, 1 - y, 1 - z$).

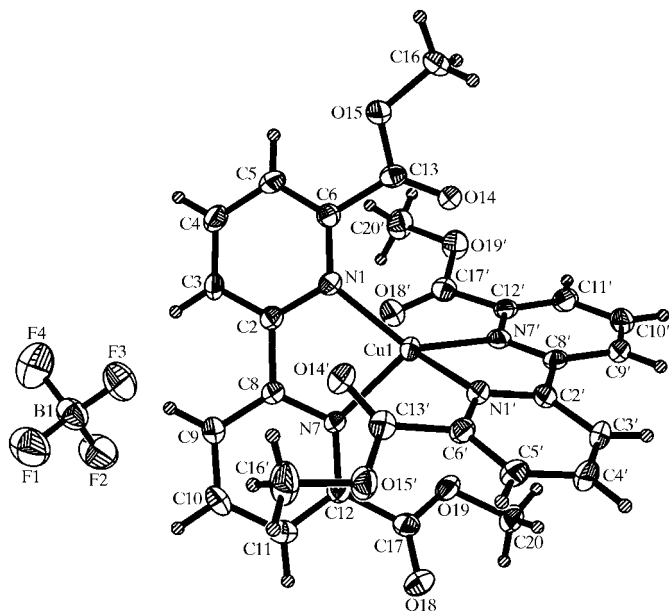


Figure 2
A view of the structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

coplanarity of the pyridyl rings of the free ligand is also lost on complexation, with an increase in the distortion of the ester groups with respect to the pyridyl rings, resulting from the increased steric constraints of the complex. The C=O and C—O bond lengths of the ester groups in both the free and complexed ligand show no significant differences, further supporting the absence of ester complexation.

It is interesting to compare the twisted arrangement of the dimethyl 2,2'-bipyridine-6,6'-dicarboxylate ligand in (II) with previously reported examples. Two N—C—N torsion angles of 10.4 (5) and 25.1 (6)° are observed for these ligands in complex (II), revealing a significantly greater twist than observed in the three structures of metal complexes of dimethyl 2,2'-bipyridine-6,6'-dicarboxylate (Anderberg *et al.*, 2002; Kinnunen *et al.*, 2000, 2002) reported prior to this study (average C—N—N—C torsion angles of *ca* 5°). The twist in (II) is also greater than that observed in bis(2,2'-bipyridine)copper(I) trifluoromethanesulfonate (Tomislav, 2006) and the analogous perchlorate salt (Munakata *et al.*, 1987), in which the 2,2'-bipyridine ligands remain essentially planar, with average C—N—N—C torsion angles of 2.9 and 1.8°, respectively.

In summary, single-crystal X-ray structures of dimethyl 2,2'-bipyridine-6,6'-dicarboxylate and its copper(I) complex, *viz.* bis(dimethyl 2,2'-bipyridine-6,6'-dicarboxylato)copper(I) tetrafluoroborate, are reported and the relative twisting of the bipyridyl unit compared.

Experimental

2,2'-Bipyridine-6,6'-dicarboxylic acid (122 mg, 0.5 mmol) and concentrated sulfuric acid (0.5 ml) in methanol (20 ml) were heated

under reflux for 3 d. The solvent was reduced to half the original volume and cooled, causing dimethyl 2,2'-bipyridine-6,6'-dicarboxylate (100 mg, 75%) to precipitate as a white crystalline solid. Single crystals suitable for X-ray diffraction were grown by slow cooling of a methanol solution of the ester. ¹H NMR (CDCl₃): δ 8.75 (*d*, 2H), 8.16 (*d*, 2H), 8.00 (*t*, 2H), 4.04 (*s*, 6H); ¹³C NMR (CDCl₃): δ 166.1, 155.9, 146.0, 138.5, 125.9, 125.3, 53.3; ES-MS: *m/z* 273 (*M*⁺ + H); IR (KBr disc, *ν*, cm⁻¹): 3476 (*s*), 1740 (*m*), 1636 (*m*), 1580 (*m*), 1295 (*w*), 1252 (*m*), 1146 (*m*), 831 (*w*), 765 (*m*), 703 (*m*), 629 (*m*). Dimethyl 2,2'-bipyridine-6,6'-dicarboxylate (13.5 mg, 0.05 mmol) in dichloromethane (5 ml) and [Cu(MeCN)₄]BF₄ (8 mg, 0.025 mmol) in acetonitrile (5 ml) were stirred together at room temperature for *ca* 30 min. The solvents were removed to give the product as a dark-red solid (15 mg). Single crystals of (II) were obtained by slow diffusion of diethyl ether into a chloroform solution of the complex. ¹H NMR (CDCl₃): δ 8.71 (*d*, 4H), 8.18 (*m*, 6H), 1.94 (*s*, 12H); FAB-MS: *m/z* 607 (*M*⁺), 335 (*M*⁺ - L); IR (KBr disc, *ν*, cm⁻¹): 3503 (*s*), 1730 (*s*), 1635 (*m*), 1592 (*m*), 1447 (*w*), 1372 (*w*), 1336 (*m*), 1310 (*w*), 1296 (*w*), 1264 (*w*), 1137 (*w*), 1116 (*m*), 1076 (*s*), 769 (*m*), 721 (*w*), 701 (*w*), 668 (*w*), 630 (*w*).

Compound (I)

Crystal data

C ₁₄ H ₁₂ N ₂ O ₄	<i>V</i> = 599.1 (3) Å ³
<i>M_r</i> = 272.26	<i>Z</i> = 2
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.4182 (15) Å	<i>μ</i> = 0.11 mm ⁻¹
<i>b</i> = 6.8889 (11) Å	<i>T</i> = 150 (2) K
<i>c</i> = 9.7931 (15) Å	0.67 × 0.61 × 0.21 mm
<i>β</i> = 109.448 (2)°	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	1360 independent reflections
3716 measured reflections	1167 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.057

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.038	92 parameters
<i>wR</i> (<i>F</i> ²) = 0.113	H-atom parameters constrained
<i>S</i> = 1.13	Δρ _{max} = 0.41 e Å ⁻³
1360 reflections	Δρ _{min} = -0.22 e Å ⁻³

Table 1

Selected bond lengths (Å) for (I).

C7—O8	1.2046 (15)	O9—C10	1.4486 (13)
C7—O9	1.3375 (13)		

Compound (II)

Crystal data

[Cu(C ₁₄ H ₁₂ N ₂ O ₄) ₂]BF ₄	<i>V</i> = 2900.1 (12) Å ³
<i>M_r</i> = 694.86	<i>Z</i> = 4
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 7.777 (2) Å	<i>μ</i> = 0.84 mm ⁻¹
<i>b</i> = 27.434 (6) Å	<i>T</i> = 150 (2) K
<i>c</i> = 13.965 (3) Å	0.26 × 0.22 × 0.07 mm
<i>β</i> = 103.254 (3)°	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	14165 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	5406 independent reflections
<i>T</i> _{min} = 0.812, <i>T</i> _{max} = 0.944	3654 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	415 parameters
$wR(F^2) = 0.137$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\max} = 0.85 \text{ e } \text{\AA}^{-3}$
5406 reflections	$\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$

H atoms were included in geometrically calculated positions, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the pyridyl CH groups, and with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms, and constrained as part of a riding model.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2003) and *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3036). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Anderberg, P. I., Harding, M. M., Luck, I. J. & Turner, P. (2002). *Inorg. Chem.* **41**, 1365–1371.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bruker (2001). *SMART* (Version 5.624), *SAINT* (Version 6.36a), *SHELXTL* (Version 6.12) and *SADABS* (Version 2.05). Bruker AXS Inc., Madison, Wisconsin, USA.
- Kinnunen, T.-J. J., Haukka, M. & Pakkanen, T. A. (2002). *J. Organomet. Chem.* **654**, 8–15.
- Kinnunen, T.-J. J., Haukka, M., Pakkanen, T. T. & Pakkanen, T. A. (2000). *J. Organomet. Chem.* **613**, 257–262.
- Munakata, M., Kitagawa, S., Asahara, A. & Masuda, H. (1987). *Bull. Chem. Soc. Jpn.* **60**, 1927–1929.
- Oxtoby, N. S., Blake, A. J., Champness, N. R. & Wilson, C. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4905–4910.
- Oxtoby, N. S., Blake, A. J., Champness, N. R. & Wilson, C. (2003). *Dalton Trans.* pp. 3838–3839.
- Oxtoby, N. S., Champness, N. R. & Wilson, C. (2005). *CrystEngComm*, **7**, 284–288.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Thébault, F., Blake, A. J., Wilson, C., Champness, N. R. & Schröder, M. (2006). *New J. Chem.* **30**, 1498–1508.
- Tomislav, P. (2006). *Acta Cryst.* **E62**, m620–m622.