Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/inoche

# A matter of greasy tails: Interdigitation of alkyl chains in free and coordinated 4'-(4-dodecyloxyphenyl)-4,2':6',4"-terpyridines

Edwin C. Constable \*, Guoqi Zhang, Catherine E. Housecroft \*, Jennifer A. Zampese

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland

### ARTICLE INFO

Article history: Received 29 August 2011 Accepted 5 October 2011 Available online 13 October 2011

Keywords: Zinc 4,2':6',4"-terpyridine Crystal structure Hydrophobic tail

## ABSTRACT

The syntheses and single crystal structures of 4'-(4-dodecyloxyphenyl)-4,2':6',4"-terpyridine, **2**, and  $[Zn_2(\mu-OAc)_4(\mathbf{2})_2]$  are reported. Crystal packing is dominated by van der Waals interactions between fully extended alkyl chains producing lamellar structures in both compounds, and appears to be the reason for the formation of crystalline  $[Zn_2(\mu-OAc)_4(\mathbf{2})_2]$  rather than a one-dimensional coordination polymer as observed for related compounds.

© 2011 Elsevier B.V. All rights reserved.

2,2':6',2"-Terpyridine (tpy) ligands substituted in the 4'-position with long hydrophobic tails (e.g. 4-octyloxyphenyl, 4-octadecycloxyphenyl) form self-organized monolayers on highly oriented pyrolytic graphite, and there is a close relationship between the structures of the monolayers and the lamellar building blocks of the 3-dimensional crystal lattice of the same compound [1]. Studies of metal complexes of these and related ligands include an assessment of the effect of the hydrophobic tail on *f*-block metal-extracting properties of the bis(tpy) metalbinding domain [2], and effects of the substituents on the emissive properties of zinc(II) and cadmium(II) complexes [3-5]. In contrast to the chelating tpy ligand, 4,2':6',4"-terpyridine presents a divergent N, N'-donor set with the central nitrogen atom typically uncoordinated [6]. Raston and coworkers have reported 4'-(4-octvloxyphenyl)-4.2':6'.4"-terpyridine, **1**, [7] its incorporation into supramolecular host-guest capsules [8,9] and the one-dimensional coordination polymer  $[ZnCl_2(1)]_n[10]$ . Here we report the synthesis of the longer homologue 4'-(4-dodecyloxyphenyl)-4,2':6',4"-terpyridine, 2, (Scheme 1) and the formation of  $[Zn_2(\mu-OAc)_4(2)_2]$ . We assess the role of the alkyl chains in the solid state structures of these complexes.

Ligand **2** was prepared in 60% yield [11] from 4-acetylpyridine and 4-dodecyloxybenzaldehyde [12] using Kröhnke methodology [13]. The base peak in the electrospray mass spectrum (m/z 516.3) was assigned to [M + Na]<sup>+</sup>, and the highest mass peak (m/z 1009.9) to [2 M + Na]<sup>+</sup>. The <sup>1</sup>H and <sup>13</sup> C NMR spectra were consistent with the structure shown in Scheme 1 and was assigned [11] using COSY, HMQC, HMBC and DEPT techniques. Structural analysis [14] revealed that **2** crystallizes in space group *P*–1 with two independent

\* Corresponding authors.

*E-mail addresses:* edwin.constable@unibas.ch (E.C. Constable), catherine.housecroft@unibas.ch (C.E. Housecroft).

molecules (Fig. 1A) in the asymmetric unit. Structurally, these differ only in the orientations of the aromatic rings. In molecule A, angles between the least squares planes of the rings containing pairs of atoms N1a/N2a, N2a/N3a and N2a/C19a are 11.20(8), 21.43(8) and 17.98(8)°. Corresponding angles for molecule B are 8.83(9), 3.92(9) and 29.30(8)°. The extended conformations of the alkyl chains allow efficient packing of the molecules into two-dimensional sheets (Fig. 1B) with van der Waals forces between the interdigitated alkyl chains dominating the packing as observed in related compounds [1,7,15] where assembly of near-planar sheets is most prevalent for the longest alkyl chains [16]. Stacking of the sheets is such that there are face-to-face  $\pi$ -interactions between tpv domains of two adjacent sheets. The next pair of sheets is slipped with respect to the first pair so that the alkyl chains of one pair lie over the tpy domains of the next. The overall structure is thereby a double layer assembly. Preliminary STM data for 2 indicate that formation of well-ordered



Scheme 1. Structure of ligand 2, and labelling scheme for NMR spectroscopic assignments.

<sup>1387-7003/\$ –</sup> see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2011.10.004



**Fig. 1.** (A) Structure of one (molecule A) of two independent molecules of **2** (ellipsoids plotted at 30% probability, and H atoms omitted). Selected bond distances and angles: N1a-C5A = 1.332(2), N1a-C1a = 1.333(2), N2a-C10a = 1.3410(18), N2a-C6a = 1.3427(18), N3a-C11a = 1.333(2), N3a-C15a = 1.338(2), C19a-O1a = 1.3573(18), O1a-C22a = 1.4348 (18) Å; C5a-N1a-C1a = 115.15(14), C10a-N2a-C6A = 117.68(12), C11a-N3a-C15a = 115.88(13), C19a-O1a-C22a = 120.07(12)°. Bond lengths and angles for the second independent molecule (molecule B) are similar; see text for torsion angles. (B) Part of one sheet of molecules of **2**; the unit cell is viewed down the *b*-axis.

monolayers on highly ordered pyrolytic graphite (HOPG) and we are currently pursuing studies using cryo-STM techniques.

By comparison with the one-dimensional polymers  $[{Zn_2(\mu-OAc)_4}]$  give  $L]_n$  obtained from reactions of  $Zn(OAc)_2 \cdot 2H_2O$  with 4'-phenyl-, 4'-(4-

bromophenyl)- or 4'-(4-methylthiophenyl)-4,2':6',4"-terpyridine [6,17], it is reasonable to assume that reaction of  $Zn(OAc)_2 \cdot 2H_2O$  with **2** will give a similar coordination polymer. Supporting this premise is the fact that treatment of  $ZnCl_2$  with 4'-(4-octyloxyphenyl)-4,2':6',4"-terpyridine



**Fig. 2.** Structure of  $[Zn_2(\mu-OAc)_4(2)_2]$  with ellipsoids plotted at 30% probability level and H atoms omitted. Important bond parameters:  $Zn_1-Zn_1^i = 2.9031(11)$ ,  $Zn_1-N_1 = 2.0431(16)$ ,  $Zn_1-O200 = 2.0471(16)$ ,  $Zn_1-O100 = 2.0559(14)$ ,  $Zn_1 O201^i = 2.0268(16)$ ,  $Zn_1-O101^i = 2.0301(15)$  Å;  $N_1-Zn_1-Zn_1^i = 178.11(4)$ ,  $N_1-Zn_1-O100 = 99.98(6)$ ,  $N_1-Zn_1-O100 = 98.72(7)$ ,  $O201^i-Zn_1-N_1 = 100.45(7)$ ,  $O101^i-Zn_1-N_1 = 99.13(6)^\circ$  The second half of the molecule is generated by the symmetry code i = -x, -y, -z.



**Fig. 3.** Part of one sheet of molecules of  $[Zn_2(\mu-OAc)_4(2)_2]$ . The unit cell is viewed along the *b* axis.

gives a helical, one-dimensional polymer [10] similar to those formed when ZnCl<sub>2</sub> reacts with other 4,2':6',4"-terpyridines [18–20]. Inspection of the crystallographic data (accessed from the Cambridge Structural Database [21]) for these structures [22] reveals that the principal effect of the octyl chains is to alter the pitch of the helix. Compound 2 reacts with two equivalents of  $Zn(OAc)_2 \cdot 2H_2O$  to give a yellow, crystalline product [23]. Whereas the  $[{Zn_2(\mu-OAc)_4}L]_n$  polymers mentioned above are poorly soluble in common organic solvents [6], the new compound is soluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. The highest mass (base) peak  $(m/z \ 1295.9)$  in the electrospray mass spectrum was assigned to  $[Zn_2(2)_4(OAc)_3]^+$ , and the isotope pattern matched that calculated. Solution <sup>1</sup>H and <sup>13</sup> C NMR spectra indicated the presence of one symmetrical ligand environment. Except for the appearance of a singlet at  $\delta$  2.11 ppm arising from the acetate groups, the <sup>1</sup>H NMR spectrum of the complex is very similar to that of 2 (both in CDCl<sub>3</sub>). Only the signals for protons H<sup>A2</sup> and H<sup>A3</sup> show any noticeable change on going from ligand to complex ( $\delta$  8.76 to 8.83 ppm, and  $\delta$  8.05 to 8.13 ppm, respectively). In the <sup>13</sup> C NMR spectrum, the signal for the C=O group was assigned from a cross-peak in the HMBC spectrum to the signal for the acetato methyl group. The electronic absorption spectra of CH<sub>2</sub>Cl<sub>2</sub> solutions of **2** and the complex both show three bands in the UV region assigned to  $\pi^* \leftarrow \pi$  transitions. The approximate doubling of  $\varepsilon_{\max}$  is consistent with the formulation  $[Zn_2(\mu-OAc)_4(\mathbf{2})_2]$  determined by X-ray diffraction.

A yellow block of  $[Zn_2(\mu-OAc)_4(2)_2]$  was selected from the bulk sample and the structural analysis [24] confirmed the discrete centrosymmetric molecule depicted in Fig. 2. Whereas the non-coordination of N2 was anticipated (see above), the fact that atom N3 does not bind zinc(II) is unexpected. The geometry of the  $\{Zn_2(\mu-OAc)_4\}$  node forces the two donors N1 and N1<sup>i</sup> to be mutually *trans*. The terpyridine domains are close to planar (angles between the least squares planes of the rings with atoms N1/N2 and N2/N3 = 2.04(8) and 12.70(11)°, and the arene substituent is twisted 24.1(4)° out of the plane of the central pyridine ring. The extended conformation of the alkyl chains imparts a Z-shaped configuration on the molecule.

Molecules of  $[Zn_2(\mu-OAc)_4(2)_2]$  assemble into 2-dimensional sheets. The packing forces are dominated by van der Waals contacts between interdigitated alkyl tails (Fig. 3) and are augmented by weak CH...N hydrogen bonds involving pendant pyridyl donor atom N3 (N3...H4a<sup>ii</sup>C4<sup>ii</sup> = 2.51, N3...C4<sup>ii</sup> = 3.440(3) Å, N3...H4a<sup>ii</sup>- $C4^{ii} = 165^{\circ}$ , symmetry code ii = 1 - x, -y, -z). The { $Zn_2(\mu-OAc)_4$ } nodes disrupt the planarity of the sheets, but the protruding methyl groups are neatly accommodated in cavities in adjacent sheets forming a 'peg-and-hole' assembly (Fig. 4A). Details of this structural motif are shown in Fig. 4B. The cavity comprises the arene and two pyridine rings of one  $[Zn_2(\mu-OAc)_4(2)_2]$  molecule, and the arene ring and part of the alkyl chain of a second molecule in the same sheet. The penetration of the Me group into the cavity results in significant, repulsive H...H contacts, and the 24.1(4)° twist of the arene ring noted above is probably in response to these interactions. The dominant packing interactions between sheets are van der Waals forces between adjacent alkyl chains. In addition there are offset face-to-face  $\pi$ -interactions between pyridine rings containing N2 and N1<sup>iii</sup> (symmetry code iii = -1 - x, -y, 1 - z), one of which is visible in the centre of Fig. 4B.



**Fig. 4.** (A) Sheets of  $[Zn_2(\mu-OAc)_4(2)_2]$  molecules are locked together by a 'peg-and-hole' assembly. The  $\{Zn_2(\mu-OAc)_4\}$  nodes are shown in green, and ligands **2** in red. (B) Detail of the 'peg-and-hole' motif. The molecule coloured orange lies beneath the other two molecules which are in the same layer.

The role of van der Waals interactions between extended alkyl chains is an expected feature of the solid state structure of **2**, and the observed lamellar structure mirrors those of related compounds. We suggest that the preference for the formation of crystalline  $[Zn_2(\mu-OAc)_4(2)_2]$  over a one-dimensional coordination polymer is driven by the dominance of van der Waals interactions between the alkyl tails of the coordinated 4'-(4-dodecyloxyphenyl)-4,2':6',4"-terpyridine ligands.

#### Acknowledgements

We thank the Swiss National Science Foundation and the University of Basel for support. GZ thanks the Novartis Foundation, formerly Ciba-Geigy Jubilee Foundation, for support. Rémy Pawlak is thanked for preliminary STM measurements.

#### Appendix A. Supplementary material

CCDC 831693 and 831694 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc. cam.ac.uk).

#### References

- E.C. Constable, H.-J. Güntherodt, C.E. Housecroft, L. Merz, M. Neuburger, S. Schaffner, Y. Tao, New J. Chem. 30 (2006) 1470.
- [2] M.G.B. Drew, P.B. Iveson, M.J. Hudson, J.O. Liljenzin, L. Spjuth, P.-Y. Cordier, Å. Enarsson, C. Hill, C. Madic, J. Chem. Soc., Dalton Trans. (2000) 821.
- [3] X. Chen, Y. Ding, Y. Cheng, L. Wang, Synthetic Met. 160 (2010) 625.
- [4] X. Chen, Q. Zhou, Y. Cheng, Y. Geng, D. Ma, Z. Xie, L. Wang, J. Lumin. 126 (2007) 81.
- [5] S.-C. Yu, C.-C. Kwok, W.-K. Chan, C.-M. Che, Adv. Mater. 15 (2003) 1643.
- [6] E.C. Constable, G. Zhang, E. Coronado, C.E. Housecroft, M. Neuburger, CrystEng-
- Comm 12 (2010) 2139 and references therein.
- [7] G.W.V. Cave, C.L. Raston, Chem. Commun. (2000) 2199.
- [8] C.L. Raston, G.W.V. Cave, Chem. Eur. J. 10 (2004) 279.
- [9] G.W.V. Cave, M.J. Hardie, B.A. Roberts, C.L. Raston, Eur. J. Org. Chem. (2001) 3227.
- 10] G.W.V. Cave, C.L. Raston, J. Supramol. Chem. 2 (2002) 317.
- [11] 4-Acetylpyridine (1.45 g, 8.00 mmol) was added to a solution of 4-dodecyloxybenzaldehyde (1.16 g, 4.00 mmol) in EtOH (20 cm<sup>3</sup>). A KOH pellet (0.45 g, 12 mmol) was added to the solution, followed by aqueous NH<sub>3</sub> (33%, 15 cm<sup>3</sup>). The reaction mixture was stirred at room temperature overnight, during which time a white suspension formed. The white solid was collected by filtration, washed well with H<sub>2</sub>O and EtOH, and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Yield: 1.19 g, 60%. m.p. 143-145 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  / ppm 8.76 (d, *J* = 6.0 Hz, 4H, H<sup>A3</sup>), 7.98 (s, 2H, H<sup>B3</sup>), 7.68 (d, *J* = 8.7 Hz, 2H, H<sup>C3</sup>), 4.02 (t, *J* = 6.5 Hz, 2H, H<sup>3</sup>), 1.81 (m, 2H, H<sup>b</sup>), 1.46 (m, 2H, H<sup>CH2</sup>), 1.40-1.18 (m, 16H, H<sup>CH2</sup>), 0.86 (t, *J* = 6.8 Hz, 3H, H<sup>c</sup>). <sup>13</sup> C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  / ppm 160.8 (C<sup>C4</sup>), 155.4 (C<sup>B2</sup>), 150.9 (C<sup>B4</sup>), 150.8 (C<sup>A2</sup>), 140.4 (C<sup>A4</sup>),

130.0 (C<sup>C1</sup>), 128.5 (C<sup>C2</sup>), 121.4 (C<sup>A3</sup>), 118.6 (C<sup>B3</sup>), 115.5 (C<sup>C3</sup>), 68.5 (C<sup>3</sup>), 32.1 (C<sup>CH2</sup>), 29.9 (C<sup>CH2</sup>), 29.85 (C<sup>CH2</sup>), 29.79 (C<sup>CH2</sup>), 29.6 (C<sup>CH2</sup>), 29.55 (C<sup>CH2</sup>), 29.4 (C<sup>b</sup>), 26.2 (C<sup>CH2</sup>), 14.3 (C<sup>C</sup>). UV/US  $\lambda_{max}/nm$  (5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, CH<sub>2</sub>Cl<sub>2</sub>), 233 ( $\epsilon$ /10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 32.8), 272 (34.7), 305sh (22.4). IR (solid, cm<sup>-1</sup>) 2913 s, 2849 m, 1591 s, 1471 m, 1390 m, 1368w, 1294w, 1173 s, 1073w, 1059w, 819 s, 719w, 693w, 662 s. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) *m/z* 1009.9 [2 M + Na]<sup>+</sup> (calc. 1009.6), 516.3 [M + Na]<sup>+</sup> (base peak, calc. 516.3). After recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH: found C 80.13, H 8.00, N 8.50; C<sub>33</sub>H<sub>39</sub>N<sub>3</sub>O requires C 80.29, H 7.96, N 8.51%.

- [12] A. Brun, G. Etemad-Moghadam, Synthesis (2002) 1385.
- [13] F. Kröhnke, Synthesis (1976) 1.
- [14]  $C_{33}H_{39}N_{30}$ , M = 493.67, colourless block, triclinic, space group P-1, a = 10.850(2), b = 14.523(3), c = 18.610(4) Å,  $\alpha = 111.285(16)$ ,  $\beta = 91.129(15)$ ,  $\gamma = 96.378(17)^\circ$ , U = 2709.8(10) Å<sup>3</sup>, Z = 4, Dc = 1.210 Mg m<sup>-3</sup>,  $\mu$ (Mo-K<sub> $\alpha$ </sub>) = 0.073 mm<sup>-1</sup>, T = 173 K, 80308 reflections collected, 10059 unique,  $R_{int} = 0.0602$ . Refinement of 8563 reflections (669 parameters) with  $I > 2\sigma$  (I) converged at final R1 = 0.0502 (R1 all data = 0.0610), wR2 = 0.1191 (wR2 all data = 0.1252), gof = 1.100.
- [15] G.W.V. Cave, C.L. Raston, J. Chem. Soc., Perkin Trans. I (2001) 3258.
- [16] Inspection of the structures and packing of 4'-(4-octyloxyphenyl)-4,2':6',4"-terpyridine (CCDC refcode XAYPOC) and 4'-(4-butyloxyphenyl)-4,2':6',4"-terpyridine (CCDC refcode ACUKAK) shows that the alkyl chains are not fully extended.
- [17] E.C. Constable, G. Zhang, C.E. Housecroft, M. Neuburger, J.A. Zampese, CrystEng-Comm 12 (2010) 2146.
- [18] M. Barquín, J. Cancela, M.J. González Garmendia, J. Quintanilla, U. Amador, Polyhedron 17 (1998) 2373.
- [19] L. Hou, D. Li, Inorg. Chem. Commun. 8 (2005) 190.
- [20] X.-Z. Li, M. Li, Z. Li, J.-Z. Hou, X.-C. Huang, D. Li, Angew.Chem. Int. 47 (2008) 6371.
- [21] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr., Sect. B 58 (2002) 389.
- [22] Conquest v. 1.13, CSD version 5.32 with updates May 2011: refcodes AJURIG, FEPRUO, GAQYUS, LOCTED, NOGFIZ, NOGFOF.
- [23] Solid Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (21.8 mg, 0.10 mmol) was added to a solution of **2** (24.7 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (9 cm<sup>3</sup>, v/v 2:1). The reaction mixture was stirred at room temperature for 30 min and the pale yellow solution was then filtered. The filtrate was left to evaporate, and after 1 week, pale yellow blocks had formed. The crystals were collected by filtration, washed with MeOH, and dried in air. Yield: 24.5 mg, 72.6% (based on **2**). m.p. 220–222 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  / ppm 8.83 (d, *J* = 5.5 Hz, 8H, H<sup>A3</sup>), 8.01 (s, 4H, H<sup>B3</sup>), 7.67 (d, *J* = 8.7 Hz, 4H, H<sup>C2</sup>), 7.05 (d, *J* = 8.7 Hz, 4H, H<sup>C3</sup>), 4.03 (t, *J* = 6.5 Hz, 4H, H<sup>A3</sup>), 2.11 (s, 6H, H<sup>MeCO2</sup>), 1.81 (m, 4H, H<sup>b</sup>), 1.47 (m, 4H, H<sup>CH2</sup>), 1.40–1.18 (m, 32H, H<sup>CH2</sup>), 0.86 (t, *J* = 6.9 Hz, 6H, H<sup>C3</sup>), 150.5 (C<sup>A2</sup>), 146.7 (C<sup>A4</sup>), 131.2 (C<sup>C1</sup>), 128.6 (C<sup>C2</sup>), 122.0 (C<sup>A3</sup>), 119.1 (C<sup>B3</sup>), 115.6 (C<sup>C3</sup>), 68.2 (C<sup>A3</sup>), 23.1 (C<sup>CH2</sup>), 29.9 (C<sup>CH2</sup>), 29.85 (C<sup>CH2</sup>), 29.82 (C<sup>CH2</sup>), 29.7 (C<sup>CH2</sup>), 29.6 (C<sup>CH2</sup>), 29.55 (C<sup>CH2</sup>), 29.4 (C<sup>b</sup>), 26.2 (C<sup>CH2</sup>), 29.29 (C<sup>MeCO2</sup>), 14.3 (C<sup>C</sup>). IR (solid, cm<sup>-1</sup>): 2922 m, 2848 m, 1635 s, 1605 m, 1596 m, 1519 m, 1423 s, 1398 m, 1296 m, 1240 m, 1180 m, 997w, 848 m, 829 s, 728w, 662 s. UV/VIS  $\lambda_{max}/nm$  (50.×10<sup>-5</sup> mol dm<sup>-3</sup>, CH<sub>2</sub>Cl<sub>2</sub>), 23.1 (c/10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 59.6), 272 (59.1), 305sh (37.4). ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) *m*/z 1295.9 [M OAc]<sup>+</sup> (base peak, calc. 1295.5), 1110.0 [Zn(2)<sub>2</sub>(OAc)]<sup>+</sup> (calc. 1109.6), 616.5 [Zn(2)(OAc)]<sup>+</sup> (calc. 616.3). Found C 65.60, H 6.67, N 62.6; C<sub>37</sub>H<sub>45</sub>N<sub>305</sub>Zn requires C 65.63, H 6.70, N 62.21%.
- [24]  $C_{74}H_{90}N_6O_{10}Zn_2$ , M = 1354.30, yellow block, triclinic, space group P-1, a = 10.753(2), b = 11.845(2), c = 14.054(3), Å,  $\alpha = 82.14(3)$ ,  $\beta = 75.51(3)$ ,  $\gamma = 81.06(3)^\circ$ , U = 1703.1(6), Å<sup>3</sup>, Z = 1, Dc = 1.320 Mg m<sup>-3</sup>,  $\mu$ (Mo-K<sub> $\alpha$ </sub>) = 0.767 mm<sup>-1</sup>, T = 173 K, 30240 reflections collected, 8163 unique,  $R_{int} = 0.0826$ . Refinement of 7666 reflections (591 parameters) with  $I > 2\sigma$  (I) converged at final R1 = 0.0418 (R1 all data = 0.0442), wR2 = 0.1151 (wR2 all data = 0.1173), gof = 1.049.