DOI: 10.1002/ejic.200600671

The Remarkable Solvent-Dependent Crystallization of the Mono- and Bis(4-pyrrol-1-ylbenzonitrile) Adducts of Bis(pentafluorophenyl)zinc

Eddy Martin,[a] David L. Hughes,[a] and Simon J. Lancaster*[a]

Keywords: Crystal structure / Zinc / Pentafluorophenyl group / Nitrile adduct / Intermolecular interaction / Arene coordination

Treatment of a toluene solution of $Zn(C_6F_5)_2$ with p-C_4H_4N–C_6H_4CN yields (p-C_4H_4N–$C_6H_4CN)_2Zn(C_6F_5)_2$, which has been structurally characterised following recrystallization from 1,2-difluorobenzene by single-crystal X-ray diffraction and possesses the expected distorted tetrahedral molecular geometry. However, crystallization from dichloromethane yields a trigonal planar complex with only one p-C_4H_4N–C_6H_4CN ligand. The three-coordinate complex forms an intermolecular dimer in the solid state through a cooperative combination of zinc–arene, offset homoaromatic and dipole–dipole interactions.

The coordination chemistry of zinc continues to enjoy healthy academic interest spurred by diverse applications in biology,[1] materials[2–4] and catalysis.[5–6] The characteristic properties of zinc are the predominance of the redox-resistant zinc(II) oxidation state, flexible coordination number and geometry, and Lewis acidity of its complexes. Four- to six-coordinate complexes of zinc are most common but there are many examples of two-coordinate zinc centres, particularly with amide, silyl and alkyl donors.[1] In contrast, mononuclear trigonal-planar complexes of zinc are relatively rare, but can be favoured through steric factors[7,8] or the combination of sterics and electrostatics as is the case for the $[Zn(C_6F_5)_3]^-$ anion.[9]

To date, all structurally characterised neutral adducts of the form ZnX_2L_n, where X is Cl, Br, I or the pseudohalide C_6F_5, and L is a monodentate Lewis base, have been shown to adopt essentially tetrahedral geometries where n is 2.[1,10] As part of our continuing investigations into the supramolecular architectures of bis(pentafluorophenyl)zinc complexes, we have structurally characterised a series of $(nitrile)_2Zn(C_6F_5)_2$ adducts.[11] We report here the unexpected isolation of the mono(nitrile) adduct (p-C_4H_4N–$C_6H_4CN)Zn(C_6F_5)_2$ and compare its solid-state structure to that of the bis(nitrile) (p-C_4H_4N–$C_6H_4CN)_2Zn(C_6F_5)_2$.

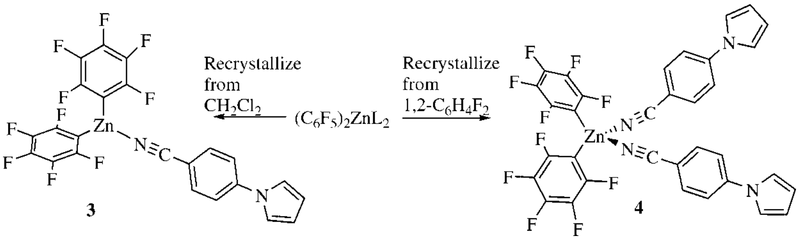
In the solid-state structure of the donor-free form of $Zn(C_6F_5)_2$ (**1**), the essentially linear geometry is perturbed only by a weak intermolecular C–F···Zn interaction.[12] Compound **1** is most conveniently prepared by the exchange between $ZnEt_2$ and $B(C_6F_5)_3$ in an aromatic solvent, from which it crystallizes with 1 equiv. of the arene.[13] The solid-state structure of the η^2-bonded toluene adduct $(MeC_6H_5)Zn(C_6F_5)_2$ (**2**) has very recently been determined.[14] This weakly bound toluene ligand can be readily displaced by Lewis bases. For example, we find that treatment of a toluene solution of **1** with 2 equiv. of the nitrogen donor ligands tBuNH$_2$, Me$_2$NH, (PhCH$_2$)$_2$NH, *cyclo*-C$_4$H$_8$NH, pyridine or benzonitrile followed by removal of toluene under reduced pressure and recrystallisation from a dichloromethane and light petroleum solvent mixture gives X-ray quality single crystals. In all but the instance discussed herein, complexes of the form $L_2Zn(C_6F_5)_2$ with distorted tetrahedral zinc environments are obtained.[11,15]

Treatment of a toluene solution of **1** with 2 equiv. of 4-(pyrrol-1-yl)benzonitrile followed by solvent removal yields a crude white solid. Subsequent crystallization from a dichloromethane and light petroleum solvent mixture at –28 °C yielded crystals (Scheme 1), which were determined by X-ray crystallography to be the mono(nitrile) complex (p-C_4H_4N–$C_6H_4CN)Zn(C_6F_5)_2$ (**3**) (Figure 1). This result was unexpected and initially assumed to be a consequence of a mistake in the reaction stoichiometry. However, despite taking great care over the reagent ratios, crystallization from dichloromethane consistently gave compound **3**. Employing identical preparative conditions but attempting crystallisation from toluene instead of dichloromethane yielded small colourless crystals that gave a different unit cell from those of **3** but did not diffract strongly enough for a full structure determination. Larger crystals, with an identical cell to those from toluene, were grown from a 1,2-difluorobenzene and light petroleum solvent mixture at +2 °C. Crystallographic analysis of this sample revealed it

---

[a] Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia,
Norwich, NR4 7TJ, UK
Fax: +44-1603-592003
E-mail: S.Lancaster@uea.ac.uk

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1.

to be the bis(nitrile) adduct (p-C_4H_4N–C_6H_4CN)$_2$Zn-(C_6F_5)$_2$ (**4**) (Figure 2). It therefore seems likely that the expected bis(nitrile) adduct is initially formed in the reaction but that recrystallization from dichloromethane yields the mono(nitrile) adduct.

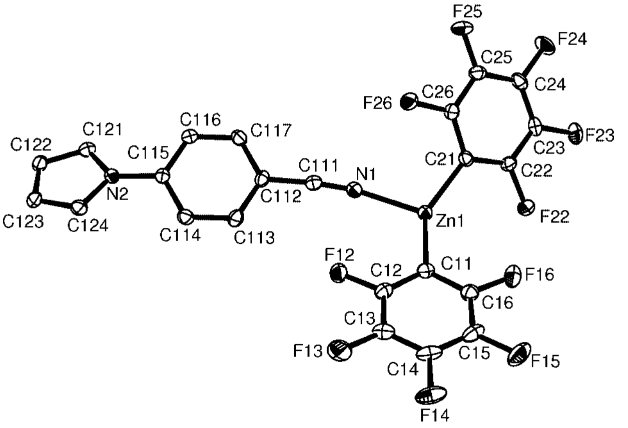


Figure 1. ORTEP representation of the molecular structure of **3** with 30% displacement ellipsoids. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; e.s.d.s are in parentheses: Zn(1)–N(1) 2.094(4), Zn(1)–C(11) 1.983(4), Zn(1)–C(21) 1.981(4), C(111)–N(1) 1.147(6), C(111)–C(112) 1.436(6), C(115)–N(2) 1.411(5); C(21)–Zn(1)–C(11) 140.1(2), C(21)–Zn(1)–N(1) 106.4(2), C(11)–Zn(1)–N(1) 108.2(2), C(111)–N(1)–Zn(1) 165.9(4), C(112)–C(111)–N(1) 174.7(5).

Complex **3** is best described as trigonal-planar, the sum of the angles about the Zn atom is 354.6° and the Zn atom is only 0.258(3) Å removed from the plane defined by C(11), C(21), and N(1). The greater steric requirement of the Zn–C_6F_5 groups explains the somewhat larger C–Zn–C vs. C–Zn–N angles. Scheme 2 shows the only other structurally characterised neutral nitrogen-ligated trigonal-planar zinc complexes we are aware of and in each case the neutral nitrogen donor is part of a bidentate ligand. The Zn–N distances for the neutral sp^2 benzimidazole and imine donors were 2.067(4), 2.089(2) 1.9805(23), and 1.962(2) Å for **I**, **II**, **III**, and **IV**, respectively. Some of these are somewhat shorter than the 2.094(4) Å found for **3**.[7,8] The average Zn–C bond length [1.982(1) Å, for **3**] is 0.03 Å less than that in [Zn(C_6F_5)$_3$]$^-$, which presumably reflects the combination of reduced steric congestion and electrostatic repulsion.[9] The dihedral angle between the aromatic planes in the coordinated nitrile ligand in **3** is 23.2(2)°.

The zinc center of the bis(nitrile) adduct **4** has an asymmetrically distorted tetrahedral coordination sphere. The 123.55(6)° C(11)–Zn–C(21) angle and the Zn–C(21) and Zn–C(11) bond lengths at 2.021(2) and 2.029(2) Å, respectively, lie well within the range observed for four-coordinate amine adducts of Zn(C_6F_5)$_2$. The average dative Zn–N bonding distance of 2.09 Å is similar to those observed for (RR′R′′N)$_2$Zn(C_6F_5)$_2$ (2.09–2.16 Å),[11] and only slightly longer than those found in (MeCN)$_2$ZnCl$_2$ (2.05 Å) and (MeCN)$_2$ZnI$_2$ (2.04 Å).[16,17] We ascribe the differences between the Zn–N distances and the dihedral angles between the aromatic rings in the ligand bonded through N(11) [2.0660(14) Å and 6.22(7)°] compared to that containing N(21) [2.1206(15) Å and 26.71(7)°] to subtle crystal packing effects. There are no other significant structural differences between the two ligands. The N(11)–Zn–N(21) angle [95.75(6)°] is somewhat smaller than those observed in the (RR′R′′N)$_2$Zn(C_6F_5)$_2$ series, doubtless as a consequence of the modest cone angle of the nitrile ligand, and is comparable to the N–Zn–N angles in (MeCN)$_2$ZnCl$_2$ and (MeCN)$_2$ZnI$_2$.[18] There is no evidence for the sort of steric congestion that would favour a three-coordinate complex.

Multinuclear NMR investigations of amine adducts of bis(pentafluorophenyl)zinc have previously indicated solution-phase equilibria involving rapid exchange of free and coordinated amine [Equation (1)]. Addition of further equivalents of amine produced a movement in the observed ^{1}H chemical shifts towards the values for the free amine, but very little change to the ^{19}F resonances of the Zn–C_6F_5 groups, which we interpreted as the equilibrium strongly favouring the four-coordinate complex.[11] This is consistent with simple thermodynamic considerations favouring the four-coordinate adduct in which two dative bonds have been formed. Regardless of the position of the solution equilibrium, the four-coordinate complexes had invariably been observed to crystallize preferentially until the isolation of **3**.

For comparison we conducted a variable-temperature ^{1}H and ^{19}F NMR study of complex **4** (an analogous study with complex **3** was not possible because of its poor solubility in toluene). The ^{19}F MMR spectrum of a [D$_8$]toluene solution barely changed on cooling from 20 to –60 °C. In contrast,

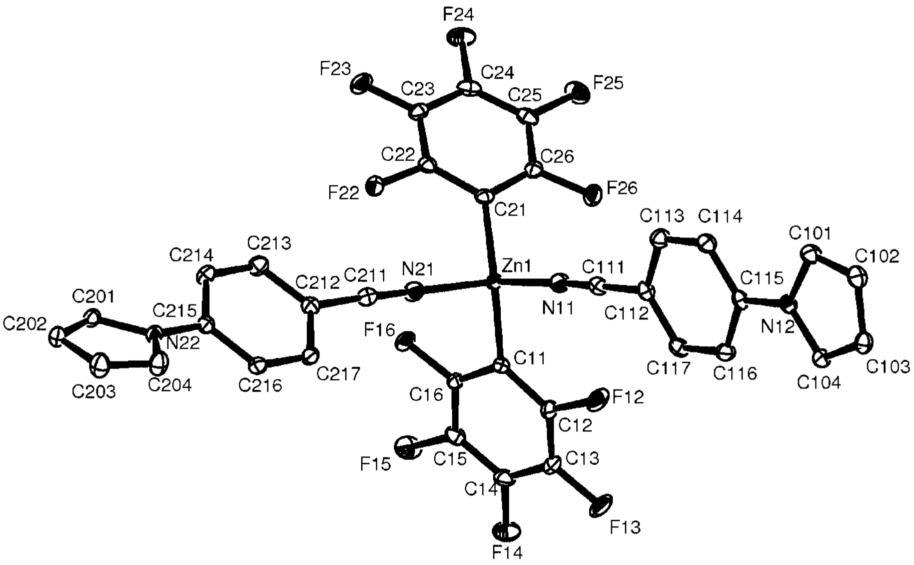
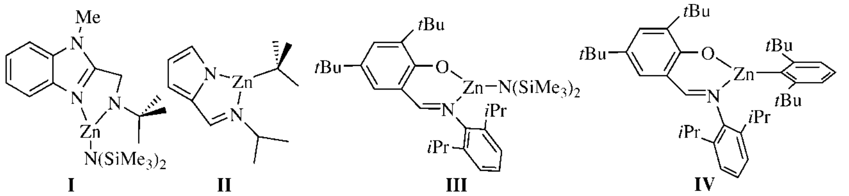


Figure 2. ORTEP representation of the molecular structure of **4** with 30% displacement ellipsoids. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]; e.s.d.s are in parentheses: Zn(1)–N(11) 2.0660(14), Zn(1)–N(21) 2.1206(15), Zn(1)–C(21) 2.0209(15), Zn(1)–C(11) 2.0292(16), C(111)–N(11) 1.139(2), C(111)–C(112) 1.437(2), C(115)–N(12) 1.409(2), C(211)–N(21) 1.143(2), C(211)–C(212) 1.437(2), C(215)–N(22) 1.412(2); C(21)–Zn(1)–C(11) 123.55(6), C(21)–Zn(1)–N(11) 114.80(6), C(11)–Zn(1)–N(11) 107.92(6), C(21)–Zn(1)–N(21) 105.58(6), C(11)–Zn(1)–N(21) 104.96(6), N(11)–Zn(1)–N(21) 95.75(6), Zn(1)–N(11)–C(111) 175.60(14), N(11)–C(111)–C(112) 179.4(2), Zn(1)–N(21)–C(211) 174.76(14), N(21)–C(211)–C(212) 176.54(17).



Scheme 2.

the chemical shifts of the ^{1}H resonances exhibited significant temperature dependence (Supporting Information). However, there was no sign of decoalescence down to –60 °C and therefore no indication for the position of this equilibrium (1).

$$(C_6F_5)_2ZnL + L \rightleftharpoons (C_6F_5)_2ZnL_2 \qquad (1)$$

Analysis of the crystal packing for complex **3** suggests a possible explanation for its preferential crystallisation. In the solid state, molecules of **3** are closely paired about centres of symmetry (Figure 3), in such a fashion that the p-C_4H_4N–C_6H_4CN ligand of one molecule runs parallel and in the opposite direction to that of the associated molecule. As well as counter-aligning the two ligand dipoles, this arrangement also leads to an offset homoaryl interaction between the phenyl rings. The centroid···centroid distance is 3.71 Å and the centroid–plane separation is 3.37 Å. The supramolecular motif in which hydroaromatics form offset pairs or stacks has been well documented.[19,20] Nevertheless, we believe that two short zinc–pyrrole ring contacts are most significant in directing this intermolecular pairing. The Zn–C(122′) distance is 2.73 Å, which is well within the sum of the van der Waals radii (ca. 3.1 Å), while the distances to C(121′) and C(123′) are in excess of 3 Å. The Zn···π interaction in **3** is evidently weaker than those reported for $(C_6F_4\text{-}2\text{-}C_6F_5)_2Zn\cdot$(toluene) in which there is a close [2.524(3) Å] contact to one arene carbon atom, and for **2** in which two contacts of 2.784(2) and 2.685(2) Å were found.[14] It is, however, strikingly similar to the Zn···π interaction observed in the solid-state structure of **II**, which also forms an intermolecular dimer with a 2.715(3) Å contact between the zinc atom and the carbon atom in the 3-position of the pyrrolyl ring.[7c]

We propose that this intermolecular association yields a species which is significantly less soluble in dichloromethane than complex **4**, and crystallizes out, thereby driving the equilibrium to the "three-coordinate" complex. In 1,2-difluorobenzene solution presumably either the formation of the intermolecular dimer is inhibited or perhaps more likely it is no longer significantly less soluble than the four-coordinate adduct **4**.

In summary, during the course of a structural survey of bis(nitrile) adducts of bis(pentafluorophenyl)zinc, an unusual and surprising example of a three-coordinate complex, (p-C_4H_4N–C_6H_4CN)$Zn(C_6F_5)_2$, was isolated from dichloromethane solution and structurally characterised.

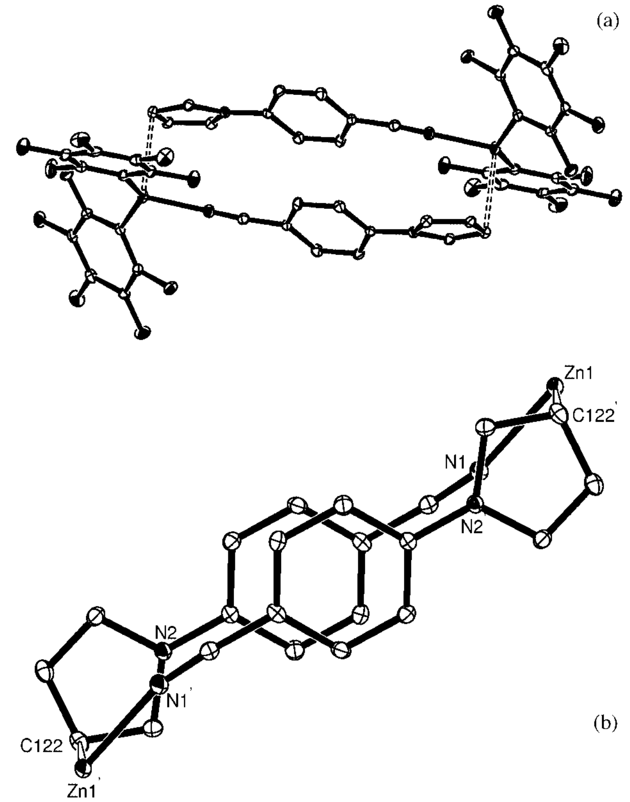


Figure 3. ORTEP representations of (a) the intermolecular dimer of **3** and (b) the alignment of the two interacting fragments projected on to the plane of the C_6 ring (the displacement ellipsoids are at 30% probability and the hydrogen atoms have been omitted for clarity).

The driving force for its crystallization is thought to be intermolecular dimerisation predominantly through Zn···π interactions.

Experimental Section

General: All experimental procedures were conducted using standard Schlenk techniques under anhydrous and anaerobic conditions. [21] The toluene adduct of bis(pentafluorophenyl)zinc was prepared according to a literature procedure.[13] 4-(Pyrrol-1-yl)benzonitrile was prepared from 4-aminobenzonitrile and 2,5-dimethoxytetrahydrofuran in refluxing acetic acid according to a modified literature procedure.[22] ^{1}H and ^{19}F NMR chemical shifts are referenced to the residual solvents and $CFCl_3$ respectively.

(p-C_4H_4N–C_6H_4CN)Zn(C_6F_5)$_2$ (3): A solution of (MeC_6H_5)-Zn(C_6F_5)$_2$ (0.44 g, 0.9 mmol) in toluene (10 mL) was treated with p-C_4H_4N–C_6H_4CN (0.3 g, 1.8 mmol). The reaction mixture was stirred for 30 min before being filtered to separate a small amount of solid material. The volatiles were removed under reduced pressure and the residue was purified by crystallisation from a mixture of dichloromethane and light petroleum at –28 °C to afford colourless crystals of **3** (0.30 g, 0.52 mmol, 58%). Crystals suitable for single-crystal X-ray diffraction required a further recrystallization step. $C_{23}H_8F_{10}N_2Zn$ (567.69): calcd. C 48.66, H 1.42, N 4.93; found C 47.92, H 1.24, N 5.30. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.76 (d, $^3J_{\text{H-H}}$ = 8.1 Hz, 2 H, Ar), 7.54 (d, $^3J_{\text{H-H}}$ = 8.7 Hz, 2 H, Ar), 7.19 (t, $^3J_{\text{H-H}}$ = 2.1 Hz, 2 H, Pyr), 6.41 (t, $^3J_{\text{H-H}}$ = 2.1 Hz, 2 H, Pyr) ppm. ^{19}F NMR (282 MHz, CD_2Cl_2): δ = –162.79 to –162.81 (m, 4 F, o-F), –157.06 (t, $^3J_{\text{F-F}}$ = 19.8 Hz, 2 F, p-F), –118.99 to –118.78 (m, 4 F, m-F) ppm.

(p-C_4H_4N–C_6H_4CN)$_2$Zn(C_6F_5)$_2$ (4): Compound **4** was prepared according to precisely the same experimental method prior to crystallization as compound **3**. The crude solid was crystallised from a mixture of 1,2-difluorobenzene and light petroleum at +2 °C affording colourless crystals of **4** (0.65 g, 0.88 mmol, 98%) suitable for X-ray analysis. $C_{34}H_{16}F_{10}N_4Zn$ (735.89): calcd. C 55.49, H 2.19 N 7.61; found C 54.94, H 2.14, N 7.91. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.41 (t, $^3J_{\text{H-H}}$ = 2.1 Hz, 2 H) 7.19 (t, $^3J_{\text{H-H}}$ = 2.1 Hz, 2 H), 7.56 (d, $^3J_{\text{H-H}}$ = 8.7 Hz, 2 H), 7.82 (d, $^3J_{\text{H-H}}$ = 8.7 Hz, 2 H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –163.6 to –163.4 (m, 4 F, o-F), –158.7 (t, $^3J_{\text{F-F}}$ = 17 Hz, 2 F, p-F), –119.0 (d, $^3J_{\text{F-F}}$ = 18 Hz, 4 F, m-F) ppm.

X-ray Analyses: Intensity data for crystals of **3** and **4** were collected with an Oxford Diffraction Xcalibur-3 CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and graphite monochromator. Data were processed using the CrysAlis-CCD and -RED programs.[23] The structures were determined by direct methods in SHELXS and refined using full-matrix least squares with SHELXL.[24] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms were taken from ref.[25] The analysis process was run through WinGX.[26] CCDC-615024 (**3**) and -615025 (**4**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure and Refinement Data for 3: $C_{23}H_8F_{10}N_2Zn$, F_W = 567.7 g mol^{-1}; monoclinic, $P2_1/c$, a = 6.8993(3), b = 20.4167(8), c = 14.2444(16) Å, β = 93.691(6)°, V = 2002.3(3) Å^3, Z = 4, T = 140(1) K, $\rho_{\text{calcd.}}$ = 1.883 Mg/m^3, μ(Mo-K_α) = 1.335 mm^{-1}, F(000) = 1120; colourless prism 0.35×0.30×0.15 mm. The total number of reflections, recorded to $\theta_{\max}$ = 27.5°, was 25382, of which 4550 were unique (R_{int} = 0.041); 3803 were "observed" with $I > 2\sigma_I$. Final R factors: wR_2 = 0.132 and R_1 = 0.066 for all 4550 reflections weighted, $w = [\sigma^2(F_o^2) + 11.38\ P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$; for the "observed" data only, R_1 = 0.055. Largest residual electron density 1.69 e·Å^{-3}, located close to C(123).

Crystal Structure and Refinement Data for 4: $C_{34}H_{16}F_{10}N_4Zn$, F_W = 735.9 g mol^{-1}; triclinic, $P\bar{1}$, a = 8.0378(5), b = 14.0455(7), c = 14.5510(9) Å, α = 114.357(6), β = 91.807(5), γ = 97.603(5)°, V = 1476.60(15) Å^3, Z = 2, T = 140(1) K, $\rho_{\text{calcd.}}$ = 1.655 Mg/m^3, μ(Mo-K_α) = 0.928 mm^{-1}, F(000) = 736; colourless prism 0.59×0.33×0.30 mm. The total number of reflections, recorded to $\theta_{\max}$ = 25°, was 16139, of which 5174 were unique (R_{int} = 0.022); 4726 were "observed" with $I > 2\sigma_I$. Final R factors: wR_2 = 0.063 and R_1 = 0.026 for all 5174 reflections weighted, $w = [\sigma^2(F_o^2) + (0.0338P)^2 + 0.589P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$; for the "observed" data only, R_1 = 0.023. Largest residual electron density 0.36 e·Å^{-3}, located close to Zn(1).

Supporting Information (see footnote on the first page of this article): Figure showing the temperature dependence of the ^{1}H NMR chemical shifts of a [D$_8$]toluene solution of complex **4**.

Acknowledgments

E. M. wishes to thank UEA for a PhD scholarship and Oxford Diffraction Ltd. for a CASE award. We are grateful for support from the Engineering and Physical Sciences Research Council.

---

[1] S. J. Archibald, *Comprehensive Coordination Chemistry II*, Elsevier-Pergamon, Oxford, **2004**, vol. 6, p. 1148.

[2] a) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511; b) O. Maury, H. Le Bozec, *Acc. Chem. Res.* **2005**, *38*, 691.

[3] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.

[4] A. Erxleben, *Coord. Chem. Rev.* **2003**, *246*, 203.

[5] M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018.

[6] B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229.

[7] a) M. S. Chinn, J. Chen, *Inorg. Chem.* **1995**, *34*, 6080; b) M. H. Chisholm, J. C. Gallucci, H. Zhen, *Inorg. Chem.* **2001**, *40*, 5051; c) J. Lewiński, M. Dranka, I. Kraszewska, W. Sliwiński, I. Justyniak, *Chem. Commun.* **2005**, 4935.

[8] For an oxygen-ligated three coordinate dialkylzinc compound, see: H.-J. Gais, G. Bülow, G. Ranbe, *J. Am. Chem. Soc.* **1993**, *115*, 7215.

[9] S. Garratt, A. Guerrero, D. L. Hughes, M. Bochmann, *Angew. Chem. Int. Ed.* **2004**, *43*, 2166.

[10] a) M. Weidenbruch, M. Herrndorf, A. Schäfer, S. Pohl, W. Saak, *J. Organomet. Chem.* **1989**, *361*, 139; b) V. W. Day, D. H. Campbell, C. J. Michejd, *J. Chem. Soc. Chem. Commun.* **1975**, 118.

[11] A. J. Mountford, S. J. Lan caster, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse, M. E. Light, *Organometallics* **2006**, *25*, 3837.

[12] Y. Sun, W. E. Piers, M. Parvez, *Can. J. Chem.* **1998**, *76*, 513.

[13] D. A. Walker, T. J. Woodman, D. L. Hughes, M. Bochmann, *Organometallics* **2001**, *20*, 3772.

[14] A. Guerrero, E. Martin, D. L. Hughes, N. Kaltsoyannis, M. Bochmann, *Organometallics* **2006**, *25*, 3311.

[15] E. Martin, C. Spendley, A. Mountford, D. L. Hughes, S. J. Coles, P. N. Horton and M. B. Hursthouse, manuscript in preparation.

[16] V. K. Bel'sky, N. R. Streltsova, B. M. Bulychev, P. A. Storozhenko, L. V. Ivankina, A. I. Gorbuvnov, *Inorg. Chim. Acta* **1989**, *164*, 211.

[17] F. Raubacher, F. Weller, *Z. Kristallogr.* **1996**, *211*, 576.

[18] The intermolecular interactions in molecule **4** and a series of pyridine- and benzonitrile-derived adducts will be discussed in ref.[15]

[19] S. Lorenzo, G. R. Lewis, I. Dance, *New J. Chem.* **2000**, *24*, 295.

[20] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525.

[21] For further details on experimental methodology, see ref.[11]

[22] I. Sanchez, M. D. Pujol, *Tetrahedron* **1999**, *55*, 5593.

[23] Programs CrysAlis-CCD and -RED, Oxford Diffraction Ltd., Abingdon, UK, **2005**.

[24] G. M. Sheldrick, *SHELX-97, Programs for crystal structure determination (SHELXS) and refinement (SHELXL)*, University of Göttingen, Germany, **1997**.

[25] *International Tables for X-ray Crystallography*, Kluwer Academic Publishers, Dordrecht, **1992**, vol. C, p. 500, 219 and 193.

[26] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

Received: July 18, 2006