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## A systematic study of ligand intermolecular interactions in crystals of copper(II) complexes of bidentate guanidino derivatives

Michael M. Bishop <sup>a,b</sup>, Simon J. Coles <sup>c</sup>, Leonard F. Lindoy <sup>a,\*</sup>, Andrew Parkin <sup>d</sup>

<sup>a</sup> Centre for Heavy Metals Research, School of Chemistry, University of Sydney, NSW 2006, Australia

<sup>b</sup> Sydney Grammar School, College Street, Darlinghurst, NSW 2010, Australia

<sup>c</sup> EPSRC National Crystallography Service, School of Chemistry, University of Southampton, Southampton SO171BJ, UK

<sup>d</sup> Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

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Dedicated to Professor M. Mingos FRS - An outstanding chemist.

## Abstract

The synthesis and X-ray structures of copper(II) complexes of the bidentate ligands, N-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-N'-phenylguanidino, 2-uanidinobenzimidazolo and N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2-yl)guanidino, are reported. These complexes, which possess potential doublet (DA) or triplet (DAD) hydrogen bonding motifs, can form supramolecular structures based on synthons involving hydrogen bonding or phenyl embraces. The changes in supramolecular structure resulting from small changes in ligand structure, as well as from the use of different solvents for their crystallisation, are examined. The structures adopted are compared with others reported previously for complexes of related ligands.

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Keywords: Copper(II); X-ray structure; Supramolecular array

## 1. Introduction

In recent times there has been a growing interest in the rational design of molecular frameworks containing transition metal complexes both by the formation of coordination polymers [1–4] in which metal ions link individual units throughout the structure or, more recently, by employing hydrogen bonding and other weak interactions between the metal-coordinated ligands [5–14].

In earlier papers we have described systems of the latter type in which a number of transition metal complexes have been incorporated into supramolecular arrays through the use of complementary hydrogen bonding motifs to link the metal-containing units [15–22].

Recently, as part of these studies, we reported the synthesis and structures of complexes of the related bidentate ligands, N-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2yl)alkanimidamido (where alk = Me, Et), methyl N-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamato and N,N-dimethyl-N'-(4-oxo-5,5-diphenyl-4,5-dihydro-1Himidazol-2-yl)guanidino (Scheme 1; Ib-e) [21,22]. These ligands readily form neutral pseudo-macrocyclic complexes with self-complementary DA hydrogen bonding motifs and were shown to be well suited to structural studies of supramolecular interactions in crystals of divalent transition metal complexes (see Scheme 2). Where linking of the potential doublet hydrogen bonding motifs was not prevented by solvation of the motif or by the steric requirements of substituents on the ligand, the individual complex units were observed to link together into chains by  $R_2^2(8)$  hydrogen bond patterns. While the complexes within the hydrogenbonded chains were often approximately coplanar, twisting

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Tel.: +61 2 935 14400; fax: +65 2 9351 3329. *E-mail address:* lindoy@chem.usyd.edu.au (L.F. Lindoy).



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of the chains also occurred in specific cases. Conformational changes within the ligands necessary to optimise the hydrogen bonding interactions were also observed. Where



X	Y	L	M <sup>2+</sup>	other		ref
Me	-	DMSO	Cu		1	[18]
Et	-	-	Cu		2a	[18]
Et	-	-	Cu	2 DMSO	2b	[18]
OMe	Н	-	Cu	2 ClO <sub>4</sub> , 2 MeOH	<b>3</b> a	[19]
OMe	-		Cu	МеОН	3b	[19]
OMe	-	DMSO	Cu		3c	[19]
OMe	-	-	Cu	2 DMSO	3d	[19]
NMe <sub>2</sub>	-	_	Cu	2 DMSO	<b>4</b> a	[19]
NMe <sub>2</sub>		-	Ni	2 DMSO	4b	[19]
NHPh	-	-	Cu	2 (1,8–naphthalimide)	5a	
NHPh	-	-	Cu	2 PhCN	5b	
NHPh	-	-	Cu	2 DMF	5c	

hydrogen bonding of the neutral complexes was not observed, the complexes formed approximately planar chains. In these the complex units were linked instead by phenyl embraces involving offset face-to-face (OFF), edgeto-face (EF) or aromatic CH-to- $\pi$  facial (CH $\pi$ ) interactions in complementary motifs involving two diphenyl moieties such as  $OFF(EF)_2$  and  $OFF(CH\pi)_2$ . It is worth noting in this context that the most advantageous intermolecular C-C distance is not the sum of the van der Waals radii (3.4 Å) but some 0.3–0.4 Å longer. For offset face-to-face interactions the distance is even greater. In fact, the intermolecular potential becomes zero, or slightly destabilising, at the van der Waals distance [23,24]. Different crystallisation solvents also gave rise to different supramolecular structures with molecules of solvent incorporated in different ways.

In the study now reported, relative to our previous study [22] we have changed the potential hydrogen bonding motif from a doublet to a triplet (DAD) in its corresponding bisligand copper(II) complex by employing the new ligand N-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-N'-phenylguanidine (Scheme 1; Ia); in the process we have also introduced another phenyl group to each ligand.

Two experiments involving the complexes of this ligand were undertaken. In the first, hydrogen-bonded chain formation was prevented by co-crystallisation of the copper complex with 1,8-naphthalimide, which contains a complementary ADA triplet motif. Stacking interactions and the arrangement of the phenyl motifs were then examined. The second experiment involved exploitation of the fact that, although the triplet DAD motifs on the complexes are not self-complementary, there are two self-complementary doublet hydrogen bonding motifs possible (Scheme 3). In order to investigate whether interchange between these modes might occur, the effect of crystallisation of the respective complexes from different solvents on chain formation was probed. The influence of the additional (third) phenyl group present in this ligand on the arrangement adopted in the solid state is also discussed.

The assembly of related complexes of the anionic forms of 2-guanidinobenzimidazole (II) and N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2-yl)guanidine (III) were also investigated for comparison with the above.



#### 2. Experimental

## 2.1. 4-Oxo-5,5-diphenyl-4,5-dihydro-1H-imidazol-2ylcyanamide

This was prepared in good yield (66%) from benzil and dicyandiamide as described previously [25].

## 2.2. N-(4-Oxo-5,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-N'-phenylguanidine (Ia)

## 2.2.1. Method A

1-Phenylbiguanide (1.77 g, 10 mmol) was added to a hot solution of KOH (0.62 g, 10 mmol) in absolute ethanol (70 mL). To this mixture was slowly added benzil (2.10 g, 10 mmol) and the resulting mixture was then heated under reflux for 4 h. The volume was reduced on a rotary evaporator to 25 mL and water was added dropwise to the hot solution. Once the solution became cloudy, the solution was allowed to cool while triturating. The white solid so obtained was isolated by filtration, recrystallised from methanol, then dried in a desiccator over silica gel. Yield 1.74 g, 47%. Anal. Calc. for C<sub>22</sub>H<sub>19</sub>N<sub>5</sub>O: C, 71.52; H, 5.18; N, 18.96. Found: C, 71.34; H, 5.02; N, 18.90%.

#### 2.2.2. Method B

The above product may also be prepared by heating 4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-ylcyanamide and aniline hydrochloride in *n*-butanol at the reflux temperature for 8 h, as reported previously for the analogous reaction employing *p*-toluidine hydrochloride [26]. Yield 0.18 g, 13%.

## 2.3. Bis(N-(4-oxo-5,5-diphenyl-4,5-dihydro-1H-imidazol-2yl)-N'-phenylguanidino)copper(II) (5)

Ligand Ia (0.369 g, 1 mmol) was dissolved in hot methanol (20 mL). To this solution was added an aqueous

Table 1 Crystallographic Data ammoniacal solution of copper(II) chloride-2-water (0.085 g, 0.5 mmol). The mixture was heated with stirring for 15 min after which the purple solid that formed was filtered off, washed with hot methanol  $(3 \times 3 \text{ mL})$  and dried in air. Yield: 0.275 g, 69%.

## 2.4. [Bis(N-(4-oxo-5,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-N'-phenylguanidino)copper(II)(1,8-naphthalimide)<sub>2</sub>] (5a)

1,8-Naphthalimide (0.0127 g, 64 mmol) was dissolved in DMF (2 mL) and **5** (0.0255 g, 32 mmol) was added. Small crystals formed on standing in near quantitative yield. *Anal.* Calc. for  $C_{68}H_{50}CuN_{12}O_6$ : C, 68.36; H, 4.22; N, 14.07. Found: C, 68.13; H, 4.44; N, 14.10%.

The above product was recrystallised from benzonitrile to yield crystals, **5b**, which were left in the growth solution until used for X-ray data collection. On isolation, these crystals lost one equivalent of benzonitrile when dried in a desiccator over silica gel. *Anal.* Calc. for  $C_{44}H_{36}Cu N_{10}O_2 \cdot 0.5C_6H_5CN$ : C, 66.96; H, 4.56; N, 17.27. Found: C, 66.98; H, 4.86; N, 17.30%.

Crystallisation of **5** from DMF gave crystals, **5c**, which were dried in a desiccator over silica gel to yield the di-DMF solvate. *Anal.* Calc. for  $C_{44}H_{36}CuN_{10}O_2 \cdot 2DMF$ : C, 63.44; H, 5.32; N, 17.76. Found: C, 63.25; H, 5.61; N, 17.76%.

When **5** was crystallised from DMSO a corresponding di-DMSO solvate was obtained after drying in a desiccator over silica gel. *Anal.* Calc. for  $C_{44}H_{36}CuN_{10}O_2 \cdot 2DMSO$ : C, 60.26; H, 5.06; N, 14.65. Found: C, 60.24; H, 5.05; N, 14.75%.

# 2.5. $[Bis(2-guanidinobenzimidazolo)copper(II)(1,8-naphthalimide)_2] \cdot 2dimethylsulfoxide (6)$

Precursor bis(2-guanidinobenzimidazolo)copper(II) was prepared in 66% yield by the addition of an ammoniacal

	5a	5b	5c	6	7
Formula of the refinement model	C68H50CuN12O6	C <sub>54,50</sub> H <sub>43,50</sub> CuN <sub>11,50</sub> O <sub>2</sub>	C50H50CuN12O4	C44H42CuN12O6S2	C <sub>28</sub> H <sub>34</sub> CuN <sub>10</sub> O <sub>3</sub>
Model molecular weight	1194.74	955.05	946.57	962.56	622.20
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (#2)	Pbcn (#60)	$P2_1/c$ (#14)	C2/c (#15)	$P\bar{1}$ (#2)
a (Å)	10.9025(7)	16.139(2)	28.0687(8)	23.2421(15)	9.0123(1)
$b(\mathbf{A})$	11.9168(8)	19.601(3)	8.4811(2)	7.5572(4)	12.2308(2)
c (Å)	12.2807(8)	28.809(4)	19.7886(4)	25.4613(18)	13.6773(2)
α (°)	74.624(4)	90.000	90.000	90.000	81.3841(5)
β (°)	75.938(4)	90.000	101.0343(7)	109.897(4)	87.6577(6)
γ (°)	65.560(4)	90.000	90.000	90.000	81.461(1)
$V(\text{\AA}^3)$	1384.35(16)	9114(2)	4623.7(2)	4205.2(5)	1473.81(4)
$D_{\rm C} (\rm g  cm^{-3})$	1.433	1.392	1.360	1.520	1.402
Z	1	8	4	4	2
Temperature (K)	150(2)	150(2)	120	150(2)	120
$\mu(Mo K\alpha) (mm^{-1})$	0.464	0.538	0.53	0.685	0.79
Residuals $R_1(F)$ , $wR_2(F^2)$	0.0546, 0.1400	0.0568, 0.1125	0.0477, 0.1181	0.0579, 0.1399	0.0368, 0.0834

Table 2		
Hydrogen	bond	Summary

Donor	Hydrogen	Acceptor	D–H (Å)	H–A (Å)	D-A (Å)	DHA angle (°)
5a						
N(2)	H(2)	O(3)	0.88	1.95	2.797(3)	161.9
N(4)	H(4)	O(2)	0.88	2.07	2.942(3)	168.3
N(6)	H(6A)	N(3)	0.88	2.14	3.022(3)	177.2
N(5)	H(5)	$O(1)^a$	0.88	1.93	2.720(3)	148.7
5 <i>b</i>						
N(7)	H(7)	$N(3)^{b}$	0.88	2.21	3.019(6)	153.7
N(2)	H(2)	$N(8)^{c}$	0.88	2.11	2.942(6)	157.0
N(5)	H(5)	O(2)	0.88	2.10	2.842(5)	142.0
N(10)	H(10)	O(1)	0.88	2.10	2.837(5)	141.0
N(4)	H(4)	N(11)	0.88	2.50	3.166(6)	132.9
5 <i>c</i>						
N(2)	H(2N)	O(3)	0.888(17)	1.868(18)	2.750(3)	172(3)
N(10)	H(10N)	O(1)	0.856(17)	1.98(2)	2.749(3)	149(2)
N(4)	H(4N)	$N(8)^d$	0.898(17)	2.129(18)	3.007(3)	166(2)
N(9)	H(9N)	$N(3)^{e}$	0.899(17)	2.081(18)	2.964(3)	167(3)
N(7)	H(7N)	O(4)	0.896(17)	1.885(18)	2.779(3)	175(3)
N(5)	H(5N)	O(2)	0.870(17)	2.00(2)	2.780(3)	148(3)
6						
N(6)	H(6N)	N(3)	0.86(3)	2.08(4)	2.940(4)	177(3)
N(4)	H(4N)	O(1)	0.82(4)	2.04(4)	2.857(3)	169(4)
N(2)	H(2NA)	O(2)	0.88(4)	2.01(4)	2.883(4)	176(3)
N(2)	H(2NB)	O(3)	0.88(4)	2.05(4)	2.929(4)	170(4)
7						
N(2)	H(2N)	O(3)	0.888(17)	1.868(18)	2.750(3)	172(3)
N(2)	H(2NA)	O(3)	0.883(15)	2.142(17)	2.933(2)	148.7(19)
O(3)	H(3OA)	N(3)	0.840(17)	2.13(2)	2.878(2)	148(3)
N(6)	H(6N)	$O(2)^{f}$	0.868(16)	2.128(16)	2.977(2)	165(2)
N(7)	H(7NA)	O(3) <sup>g</sup>	0.878(16)	2.104(18)	2.906(2)	151(2)
N(2)	H(2NB)	$N(8)^{h}$	0.885(16)	2.317(18)	3.167(2)	161(2)
O(3)	H(3OB)	$N(8)^{i}$	0.840(17)	2.26(3)	2.904(2)	134(3)
		b	0	d	i i la la f	. a

Symmetry operators:  ${}^{a}1 - x$ , 1 - y, 1 - z;  ${}^{b}-x + 3/2$ , y + 1/2, z;  ${}^{c}-x + 3/2$ , y - 1/2, z;  ${}^{d}x$ , -y + 1/2, z + 1/2;  ${}^{e}x$ , -y + 1/2, z - 1/2;  ${}^{f}x - 1$ , y, z;  ${}^{g}x$ , y + 1, z;  ${}^{h}1 - x$ , 1 - y, 1 - z;  ${}^{i}x$ , y - 1, z.

solution of copper(II) chloride to a methanol solution of 2-guanidinobenzimidazole, as previously described for the corresponding nickel(II) complex [15]. Crystals of **6** suitable for X-ray crystallography were obtained by dissolving

a mixture of 1,8-naphthalimide (0.04 g, 0.2 mmol) and the above complex (0.04 g, 0.1 mmol) in hot dimethylsulfoxide (6 mL) and allowing the solution to stand. Clusters of brown crystals of product formed in near quantitative

Table 3 Selected metal environmental geometry details for compounds 5a-c, 6 and 7

	(	Cu(1) - N(1)	Cu(1)–N(5)		Cu(1)–N(6)	Cu(1)–N(10)
Coord	ination bond (Cu–N) le	ngths in Å				
5a <sup>a</sup>	2.011(2)		1.946(2)			
5b	1.983(4)		1.920(4)		1.998(4)	1.919(4)
5c	2.0320(18)		1.9252(19)	2.0276(19)		1.9215(19)
<b>6</b> <sup>a</sup>	1.930(3)		1.941(2)	1.941(2)		
7		.9177(16)	1.9576(15)		1.9177(16)	1.9597(15)
	N(1)-Cu-N(5)	N(1)-Cu-N(6)	N(1)-Cu-N(10)	N(5)-Cu-N(6)	N(5)-Cu-N(10)	N(6)-Cu-N(10)
Coord	ination bond angles in $^\circ$					
5a <sup>a</sup>	85.94(9)	180	94.06(9)		180	
5b	87.23(17)	171.96(17)	92.92(17)	94.24(16)	168.89(18)	87.16(17)
5c	87.30(8)	178.66(8)	92.44(8)	93.22(8)	178.02(9)	87.09(8)
<b>6</b> <sup>a</sup>	88.56(11)	151.39(18)	97.20(11)		156.61(15)	
7	89.93(7)	145.03(7)	101.35(7)	101.61(7)	143.03(7)	89.09(6)

yield. Anal. Calc. for  $C_{40}H_{30}CuN_{12}O_4 \cdot 2DMSO$ : C, 54.90; H, 4.40; N, 17.47. Found: C, 54.86; H, 4.14; N, 17.16%.

## 2.6. N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2yl)guanidine (III)

Phenylbiguanide (0.885 g, 5 mmol) was suspended in absolute ethanol (20 mL) and cyclohexanedione (0.566 g, 5 mmol) was added. The yellow suspension was stirred for 20 min at room temperature and then heated under reflux for 20 min. The volume of the solution was reduced 15 mL on a rotary evaporator. The residue was transferred to a small flask and crystallisation was induced by scratching the sides of the flask; the flask was sealed and allowed to stand until crystallisation was complete. The product was isolated and air dried. Yield 0.25 g, 18%. IR 3540, 3420, 3390 cm<sup>-1</sup>; v(C=O) 1720 cm<sup>-1</sup>.

## 2.7. Bis(N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2yl)guanidino)copper(II)-1-water (7)

Ligand III (0.135 g, 0.5 mmol) was dissolved in warm ethanol (10 mL). To this solution was added an ammoniacal solution of copper(II) chloride-2-water (0.043 g, 0.25 mmol) and the mixture was allowed to stand. The dark green solid that formed was isolated, washed with  $Et_2O(1 \times 2 mL)$  and air dried. Yield 0.09 g, 29%. The product was crystallised from DMF to yield crystals that proved suitable for X-ray diffraction. The material was dried in a desiccator over silica gel before microanalysis. *Anal.* Calc.



Fig. 1. An ORTEP [36] depiction of 5a with thermal ellipsoids drawn at the 20% level.

for  $C_{28}H_{32}CuN_{10}O_2 \cdot H_2O$ : C, 54.05; H, 5.51; N, 22.52. Found: C, 54.13; H, 5.52; N, 22.45%.

The product was also recrystallised from DMSO to yield further crystals that, after drying in a desiccator over silica gel, analysed as the corresponding sesquihydrate. *Anal.* Calc. for  $C_{28}H_{32}CuN_{10}O_2 \cdot 1.5H_2O$ : C, 53.28; H, 5.59; N, 22.20%. Found: C, 53.13; H, 5.61; N, 21.80%.

#### 2.8. X-ray structure determinations

Crystallographic data for **5a**, **5b** and **6** were collected at 150 K on a Bruker SMART 1000 CCD diffractometer

equipped with an Oxford Cryosystems low temperature device [27], and using graphite monochromated Mo K $\alpha$  sealed tube radiation. Data for these three structures were integrated using SAINT [28], and an absorption correction was applied based on the method of Blessing [29] using the program SADABS [30]. Data for **5c** and **7** were collected at 120 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems low temperature device [27], and using graphite monochromated MoK $\alpha$  radiation generated using a rotating anode. Data for these two structures were integrated using the program DENZO [31], and an absorption correction was applied based on the method



Fig. 2. An ORTEP [36] depiction of 5b with thermal ellipsoids at the 20% level.



Fig. 3. An ORTEP [36] depiction of 5c with thermal ellipsoids drawn at the 20% level.

of Blessing [29], and using the program SORTAV [29]. All five structures were solved by direct methods; 5a, 5c and 7 were solved using SIR92 [32], 5b and 6 were solved using SIR97 [33]. All structures were extended and refined against  $F^2$ using full matrix least squares using the WINGX [34] and SHELXTL [35] suites of programs. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined as riding and rotating groups, with the exception of those hydrogen atoms involved in hydrogen bonding, which were freely refined with isotropic displacement parameters. Deviations from this refinement strategy are given below for individual structures. Final refinement data for all five structures are given in Table 1, and details of hydrogen bond geometry and metal environment geometry are given in Tables 2 and 3, respectively. ORTEP [36] plots are shown in Figs. 1–5.

**5a**: Hydrogen atoms involved in hydrogen bonding were observed in the Fourier difference map, then placed geometrically and refined as riding groups.

**5b**: Hydrogen atoms involved in hydrogen bonding were placed geometrically and refined as riding groups.

#### 3. Results and discussion

#### 3.1. Ligand synthesis and structure

Ligand Ia was obtained using two procedures (Scheme 4a) based on related literature syntheses [21,22]. Ligand N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2-yl)-III. guanidine, was prepared from phenylbiguanide and cyclohexanedione (which undergoes a rearrangement similar to the benzilic acid rearrangement in base) [37] (Scheme 4b). Interestingly, we obtained this product rather than the isomeric N-(4-oxo-1,3-diazaspiro[4.4]non-2-en-2-yl)-N'-phenylguanidine (IV) previously reported as the most likely structure [38,39]; the physical data presented to support the assignment of the structure of IV (microanalysis, molecular weight by mass spectrometry and spectral data, including an 8-proton multiplet corresponding to the cyclopentanylidene ring and the carbonyl IR absorption) [39] is also consistent with structure III. The carbonyl stretch in III occurs at  $1720 \text{ cm}^{-1}$ , which is higher than the  $1688 \text{ cm}^{-1}$  observed for the free ligand Ie and suggests that



Fig. 4. An ORTEP [36] depiction of 6 with thermal ellipsoids drawn at the 20% level.

the carbonyl stretch in **III** is less affected by conjugation than that of **Ie**.



3.2. Crystal packing: phenyl embraces and  $\pi$  stacking in **5a** and **6** 

The species **5a** incorporates three-component units; namely, a pseudo-macrocyclic metal complex together with two molecules of 1,8-naphthalimide, with the latter hydrogen bonded to the copper(II)-bound ligands via complementary triplet motifs (Table 2). The centro-symmetric copper complex is square-planar (Table 3) with the copper lying just 0.098 Å out of the plane defined by the rest of the metallaring N(1)–C(3)–N(3)–C(4)–N(5). The phenyl group on N(4) is *syn*, which is necessary for the formation of the hydrogen bonds mentioned above.

In earlier papers we have shown that when metal-containing motifs such as that in **5a** are prevented from forming hydrogen-bonded chains through the presence of bound solvent molecules or due to the steric nature of the ligand, chains in which the units are linked by phenyl embraces tend to form instead. The formation of the three-component unit in **5a** effectively prevents the formation of hydrogen-bonded chains and OFF(CH $\pi$ )<sub>2</sub> embraces occur that link individual units (Figs. 6 and 7). The arrangement differs from that observed in other potentially similar crystalline products (namely **2b**, **3d**, **4a** and **4b**) [21,22].

It is noted that a diphenyl group can form an OFF(CH $\pi$ )<sub>2</sub> embrace in two ways, which are perpendicular to one another. In the earlier instances (**2b**, **3d**, **4a** and **4b**) the embraces resulted in chains, represented diagramatically in Scheme 5a, in which two of the Cu–N bonds are aligned with the chain axis and adjacent Cu atoms are separated by 16 Å. In contrast, in **5a** the embrace adopts the orientation shown in Scheme 5b with the result that the adjacent Cu atoms are 14.3 Å apart. In addition to this embrace there is another OFF(CH $\pi$ )<sub>2</sub> embrace present involving one of the phenyl groups on the imidazole ring and the phenyl group attached to N(4) on the other ligand in the pseudo-macrocyclic structure (Fig. 7). These embraces link the chains into sheets that lie quasi-perpendicular to the *b*-axis.

The naphthalimide molecules in the above structure are involved in staggered stacking interactions with the ligands



Fig. 5. An ORTEP [36] depiction of 7 with thermal ellipsoids at the 20% level.



Scheme 4.



Fig. 6. A PLATON [37] depiction of the offset face to face phenyl embraces, labelled (I), linking adjacent complexes in 5a; other broken lines indicate hydrogen bonds. The 1,8-naphthalimide moieties have been omitted for clarity.



Fig. 7. A PLATON [37] depiction of the view of **5a** along the *b*-axis showing the two types of phenyl embrace present. The three complexes running from top left to bottom right are linked by embraces of type (I) as shown in Fig. 6. The second type of embrace is labelled (II). The 1,8-naphthalimide moieties are omitted for clarity; the hydrogen bonds are also not shown so that all the broken lines represent phenyl-phenyl interactions.



Scheme 5.



Fig. 8. A PLATON [37] depiction of the stacking of 1,8-naphthalimide moieties with the ligands in (a) 5a and (b) 6. The bonds in the molecules in the upper layer of the stack are shaded.

in such a way that each of the three naphthalimide rings has a ligand nitrogen atom aligned with its centroid (Fig. 8a). The naphthalimide C(27) and C(28) make an edge-to-face contact with a phenyl ring. The stacks do not run through the crystal but involve just two ligands and two naphthalimides (between which the stacking is graphite-like).

The assembly **6** was prepared to provide another example of stacking of 1,8-naphthalimide with 2-guanidinobenzimidazole, a planar ligand somewhat similar, especially in the arrangement of heteroatoms, to the ligand in **5a**; **6** differs only in detail from the nickel analogue described earlier [16]. The metal complex cannot be planar because of the steric 'clash' between the hydrogen atoms on C(7) and N(1) on opposite ligands. This results in a tetrahedral distortion from square planar geometry (Table 3) that in turn prevents formation of the stacking motif that occurs in **5a**; instead, that shown in Fig. 8b is observed.

## 3.3. Solvation by benzonitrile (5b)

When 5 was crystallised from benzonitrile, a weak hydrogen bond acceptor, crystals of 5b were obtained. In these crystals the coordination geometry of the complex shows a tetrahedral distortion from square planar but the hydrogen bonds that close the pseudo-macrocycle remain



Fig. 9. A PLATON [37] depiction of the hydrogen-bonded chains in **5b**. Notice the twisting of the complexes that form the chain and that it is the imidazole N-H that is utilised in chain formation, not the amino N-H.



Fig. 10. A PLATON [37] depiction of the hydrogen-bonded chains in **5c**; the DMF molecules have been omitted for clarity. Notice the extreme twisting of each complex with respect to its neighbours. Also note that it is the amino N–H that is utilised in chain formation; the imidazole N–H is hydrogen bonded to a DMF solvent molecule.

intact (Tables 2 and 3). The copper ion lies 0.38 and 0.34 Å, respectively, out of the planes defined by the ligand atoms N(1)-C(3)-N(3)-C(4)-N(5) and N(6)-C(25)-N(8)-C(26)-N(10).

The complexes are linked into chains, quasi-parallel with the *b*-axis, by  $R_2^2(8)$  hydrogen bonding patterns in which the imidazole nitrogen atoms N(2) and N(7) act as donors (Scheme 3a). Of the other possible donors, only N(4) is involved in a long and not very linear interaction with a benzonitrile nitrogen N(11) (Table 2). The  $R_2^2(8)$  patterns, and hence the chains, are far from planar (Fig. 9) with the plane defined by N(6)–C(25)–N(7)–N(8) making an angle of 42.5° with the plane defined by N(1)–C(3)–N(2)–N(3). The chains are stacked on top of one another in the *a* direction, with the copper ions offset.

There are two distinctly different benzonitrile sites. The molecule containing N(11) is associated with the hydrogenbonded chains and the other, containing N(12), is located on a special site and lies in a pocket surrounded by ligand phenyl groups. N(11) is involved in a long hydrogen bond with N(4). The centroid of the benzene ring lies over N(5) with the average C–N distance 3.63 Å.

An examination of 2-guanidinobenzimidazole complexes in earlier work [15,16,19] shows that in these the imidazole nitrogen is used in preference to the guanidine nitrogen as the donor in the  $R_2^2(8)$  patterns that lead to chain formation. The hydrogen bonds involving the imidazole nitrogen are also consistently shorter than those involving the guanidino nitrogen in complementary triplet motifs and, if one hydrogen bond is broken so reducing the triplet to a doublet, it is the bond involving the guanidino nitrogen.

## 3.4. Solvation by N,N-dimethylformamide (5c)

Crystallisation of 5 from DMF gives crystals of 5c, which once again contains an almost square planar copper complex, with hydrogen bonds again forming a pseudo-



Fig. 11. A PLATON [37] depiction of view along the *c*-axis showing the edge to face interactions (broken lines) between phenyl groups in **5c**; DMF molecules have been omitted for clarity, as have the hydrogen bonds.

macrocycle (Tables 2 and 3). The copper ion lies 0.12 and 0.17 Å, respectively, out of the planes defined by the ligand atoms N(1)-C(3)-N(3)-C(4)-N(5) and N(6)-C(25)-N(8)-C(26)-N(10).

The complexes are linked into chains, quasi-parallel with the *c*-axis, by  $R_2^2(8)$  hydrogen bonding patterns in which the imidazole nitrogen atoms are not involved but instead the guanidino nitrogen atoms N(4) and N(9) act as donors (Scheme 3b). The imidazole donors N(2) and N(7) are hydrogen bonded to DMF molecules, with the DMF methyl groups oriented away from the copper ion. The  $R_2^2(8)$  patterns, and hence the chains, are far from planar (Fig. 10) with the plane defined by N(10)–C(26)–N(9)–N(8) making an angle of 54.9° with the plane defined by N(5)–C(4)–N(4)–N(3).

The complexes are also linked into chains quasi-parallel to *b* by centrosymmetric pairs of EF interactions between the imidazole phenyl rings (Fig. 11); this leads to the formation of sheets of complexes, with DMF methyl to phenyl  $\pi$ -facial interactions within these sheets.

Because the chains lie directly above one another, there are channels, occupied by the DMF molecules, running through the crystal. The channels are somewhat constricted by the lack of co-planarity between complexes within the chains.

## 3.5. Bis(N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2yl)guanidino)copper(II)-1-water

The new ligand, N-(4-oxo-3-phenyl-1,3-diazaspiro[4.4]non-1-en-2-yl)guanidine, III, forms a green uncharged bis complex with copper(II) in ammoniacal solution. An X-ray diffraction study of the crystals, 7, obtained by crystallisation of the initial product from DMF is shown in Fig. 5. Individual complex units have a distorted tetrahedral geometry and are linked into extended arrays by hydrogen bonding (Tables 2 and 3). Whereas in 5 there is a carbonyl group on the ligand that leads to the formation of pseudo-macrocycles, in III there is a five-membered hydrocarbon ring leading to steric hindrance such that a square planar, or approximately square planar, coordination geometry is no longer possible. The two crystallographically distinct metallarings in each complex are approximately planar with the copper ion lying 0.08 and 0.06 Å from the planes defined by the ligand atoms in each metallaring; these planes make an angle of 55.5° with one another. There is no DMF, coordinated or hydrogen bonded to a ligand donor, in the crystal.

The *N*-phenyl groups on the ligands prevent the formation of a  $R_2^2(8)$  hydrogen bond pattern between complexes. What is observed instead is that a water molecule, which



Fig. 12. A PLATON [37] depiction of the view along the *c*-axis of 7 showing the formation of sheets by hydrogen bonding. The complexes are linked directly into chains quasi parallel to *a* by N–H···O hydrogen bonds. These chains are cross-linked indirectly by hydrogen bonding with water molecules; these linkages run quasi-parallel to *b*.



Fig. 13. A PLATON [37] depiction of the view along the b-axis of 7 showing the hydrogen bonding, quasi-parallel to c, between a pair of sheets.

has two donor and two acceptor sites, links the potentially complementary DA motifs by forming two  $R_2^2(6)$  patterns with one atom, O(3), in common. Thus, hydrogen-bonded chains, quasi-parallel to *b*, are formed, though the complexes are not directly linked. The plane defined by N(6)– C(15)–N(7)–N(8) makes an angle of 63.6° with that defined by N(1)–C(1)–N(2)–N(3). The water oxygen, O(3), lies close to the faces of the two *N*-phenyl groups. The carbonyl groups that act as hydrogen bond acceptors in coordinated (deprotonated) **Ia** to form pseudomacrocycles cannot do so in these complexes. In this latter case they are oriented so that they have the potential to link neighbouring complexes. In fact, only one of the carbonyl oxygens, O(2), does this, accepting a proton from a coordinated imino nitrogen, N(6), forming chains quasiparallel to *a*. The guanidino nitrogen, N(7), is aligned with the centroid of a phenyl ring (which has a water positioned over the other face) in the neighbouring complex in the chain. Overall, the presence of the two hydrogenbonded chains corresponds to the formation of sheets (Fig. 12).

Interestingly, the other carbonyl oxygen, O(1), is not involved in hydrogen bond formation, which would lead to a three-dimensional hydrogen-bonded array. Instead, the sheets are paired, linked by N(2)–H···N(8) $\pi$  hydrogen bonds as shown in Fig. 13.

## 4. Conclusions

In this paper we have extended the scope of our previous studies [21] of the arrays formed by neutral pseudo-macrocyclic copper(II) complexes of ligands containing a diphenylimidazolinone moiety by investigating the complexation behaviour of a related ligand bearing a potential DAD triplet hydrogen bonding motif. It was found that when the copper(II) complex of this latter system was co-crystallised with 1,8-naphthalimide, a molecule with a complementary ADA motif, the component units assembled into chains using  $OFF(CH\pi)_2$  phenyl embraces between the two phenyl substituents on the imidazole ring. Chains based on this synthon had been reported earlier for complexes incorporating potential doublet DA motifs in which steric requirements or solvation prevented the formation of hydrogen-bonded chains based on  $R_2^2(8)$  patterns. However, in the present case the orientation of the embrace with respect to the pseudo-macrocycle was different. In addition,  $OFF(CH\pi)_2$ embraces involving a third phenyl group on the ligand and one of the imidazole phenyls linked the chains into twodimensional arrays.

When the complex was crystallised in the absence of 1,8naphthalimide structure obtained consisted of twisted hydrogen-bonded chains linked by  $R_2^2(8)$  patterns formed by self-complementary DA–AD motifs. There are two ways in which a triplet DAD motif might do this and both were observed experimentally on growing the crystals from different solvents (benzonitrile and DMF); both products were found to incorporate corresponding solvent molecules. In the crystals grown from DMF, the above chains were joined into sheets by EF interactions between the imidazole phenyl rings.

In an attempt to prepare an analogous ligand without the diphenyl substitution on the imidazole ring led instead to a product incorporating a potential doublet motif. This ligand, while appearing to show the potential to form a three-dimensional hydrogen-bonded network, based on a tetrahedral coordination geometry was found, however, to yield a coordination geometry that was significantly distorted from tetrahedral. This was reflected by the assembly of a two-dimensional array. In this case, the formation of chains based on  $R_2^2(8)$  patterns was prevented by steric factors. Instead, the two DA motifs link via an intervening water molecule. Further linkages also form involving inter-complex NH···O hydrogen bonds.

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