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### Mononuclear Cu and dinuclear Cu–Ln complexes of benzimidazole based ligands including N and O donors: Syntheses, characterization, X-ray molecular structures and magnetic properties

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#### ABSTRACT

The synthesis of two mononuclear precursor copper complexes,  $[(HL^2)_2Cu]$ , **1**, and  $[(HL^3)_2Cu]$ ·H<sub>2</sub>O, **2**, and three dinuclear Cu-Ln complexes,  $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , **3**,  $[(HL^3)_2CuGd(NO_3)_3] \cdot 2(H_2O)$ , **4**, and [(HL<sup>3</sup>)<sub>2</sub>CuTb(NO<sub>3</sub>)<sub>3</sub>]·2(H<sub>2</sub>O), **5**, based on the ligands H<sub>2</sub>L<sup>1</sup> (4-bromo-2-[1-(5-bromo-2-hydroxy-3methoxybenzyl)-1*H*-benzimidazol-2-yl]-6-methoxyphenol), H<sub>2</sub>L<sup>2</sup> (2-(1*H*-benzimidazol-2-yl)-4-bromo-6-methoxyphenol) and  $H_2L^3$  (2-(1*H*-benzimidazol-2-yl)-6-methoxyphenol) are described in this contribution. The X-ray crystal structures of  $H_2L^2$ , 1, 3, 4, and 5 have been solved. The novel ligand  $H_2L^2$  crystallizes with two independent molecules in the asymmetric unit; several intermolecular hydrogen contacts connect alternate independent  $H_2L^2$  molecules into chains developing along *c*. In complex 1, two  $(HL^2)^-$  ligands chelate the copper ion through their imidazolyl nitrogen and phenoxo oxygen atoms, in a relative head to tail arrangement. The molecular structure of **3** is similar to those of the previously reported Cu–Ln complexes of  $H_2L^1$ . In the isostructural complexes 4 and 5, two  $HL^3$  ligands sandwich one  $Cu^{2+}$  ion through their N,O sites and one  $Ln^{3+}$  ion through their  $O_2$  site, implying a relative head to head arrangement, at variance with the relative head to tail arrangement of  $\mathrm{HL}^2$  in the mononuclear copper precursor 1. The magnetic properties of 1, 3, 4, and 5 have been investigated. Extended intermolecular antiferromagnetic interactions operate in complex 1 ( $(J_{Chain} = -0.8(1) \text{ cm}^{-1})$ ). Ferromagnetic interactions between Gd (S = 7/2) and Cu (S = 1/2) centers operate in complexes **3** and **4**, leading to an S = 4 ground state ( $J_{CuGd}$  = 7.2(2) cm<sup>-1</sup> for **3** and  $J_{CuGd}$  = 6.5(2) cm<sup>-1</sup> for **4**). Depopulation of the Tb Stark levels, preclude obtaining reliable information on the presence and sign of the Cu-Tb interaction in 5. These new complexes are complementary to those previously reported: the Cu-O<sub>2</sub>-Gd core is planar while deformations are borne by the ligands at variance with previous examples where the constraints were located at the Cu–O<sub>2</sub>–Gd core. The presence of two independent ligands in the Cu,Gd coordination spheres confers a degree of freedom greater than that allowed by a unique tetradentate ligand. As a result, the strength of the magnetic interaction is not solely related to the dihedral angle between the CuOO and GdOO planes in the central core.

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#### 1. Introduction

A large majority of strictly dinuclear Cu–Gd complexes exhibit a ferromagnetic behavior [1–3]. It is then of interest to link such ferromagnetic Cu–Gd units with the aim of achieving either finite

zero-dimensional (0D) or extended one-dimensional to threedimensional (1–3D) high-spin materials. The material obtained may be a single molecule magnet (SMM) [4–12], in the former case, or a single chain magnet (SCM) in the case of a 1D material [13], or a genuine ferromagnet in the latter cases [14,15]. To this end, the dinucleating ligand must include an additional free coordination site located in such a way that each copper ion is not only intra-molecularly, but also inter-molecularly, bridged to Gd ions. This strategy has allowed synthesizing tetranuclear [Cu–Gd]<sub>2</sub> species by using unsymmetrical ligands including an amide function [4,6,7], and an infinite chain of such tetranuclear components {[Cu–Gd]<sub>2</sub>]<sub>n</sub> by using ligands including amide, alcohol and phenol

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functions [13]. In both types of materials, all Cu–Gd interactions, including those mediated by the amido bridges, are ferromagnetic, thus achieving the goal pursued. However, the Cu-Gd ferromagnetic interactions mediated by the amido bridges are weaker than those involving phenoxo bridges. In our quest for dinucleating ligands promoting both intra-molecular and inter-molecular Cu-Gd bridges, we now consider the potential of (benz)imidazole function(s) for bridging metal centers upon deprotonation [16,17]. In this contribution, we describe the synthesis of two novel ligands, H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>3</sup>, two mononuclear precursor copper complexes, [(HL<sup>2</sup>)<sub>2</sub>Cu], **1**, and [(HL<sup>3</sup>)<sub>2</sub>Cu]·H<sub>2</sub>O, **2**, and three dinuclear Cu–Ln complexes,  $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , **3**,  $[(HL^3)_2CuGd$  $(NO_3)_3]\cdot 2(H_2O)$ , **4**, and  $[(HL^3)_2CuTb(NO_3)_3]\cdot 2(H_2O)$ , **5**, based on the  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$  ligands depicted in Scheme 1. The X-ray crystal and molecular structures of  $H_2L^2$ , **1**, **3**, **4**, and **5** are reported, as well as the magnetic properties of **1**, **3**, **4**, and **5**.

#### 2. Experimental section

#### 3.1. Materials

All chemicals and solvents, obtained from Aldrich, were of reagent grade and were used for the syntheses without further purification.

#### 3.2. Ligands

#### 3.2.1. H<sub>2</sub>L<sup>1</sup>

4-Bromo-2-[1-(5-bromo-2-hydroxy-3-methoxybenzyl)-1*H*-benzimidazol-2-yl]-6-methoxybenol, was prepared according to the reported experimental procedure [18]. The recrystallized material was obtained as colorless crystals. Yield 1.6 g (29%). Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3401, 2934, 1609, 1487, 1277, 1258, 1074, 758, 747. <sup>1</sup>H NMR, dmso-*d*6: 3.79 (3 H, s, OCH<sub>3</sub>, H24); 3.89 (3 H, s, OCH<sub>3</sub>, H16); 5.33 (2 H, s, CH<sub>2</sub>, H17); 6.21 (1 H, d, *J* = 2.0 Hz, CH, H23); 7.00 (1 H, d, *J* = 2.0 Hz, CH, H21); 7.09 (1 H, d, *J* = 2.1 Hz, CH, H15); 7.25 (2 H, m, CH, H6, H7); 7.27 (1 H, d, *J* = 2.1 Hz, CH, H13); 7.45 (1 H, m, CH, H8); 7.72 (1 H, m, CH, H5);



Scheme 1. Experimental route to the H<sub>2</sub>L<sup>1</sup>, H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>3</sup> ligands.

9.36 (1 H, s, OH, H19); 10.41 (1 H, s, OH, H11). <sup>13</sup>C NMR: 43.2, C17; 56.7, C24; 56.8, C16; 110.2, C22; 110.3, C14; 111.3, C8; 114.5, C21; 116.6, C13; 119.1, C10; 119.5, C5; 121.9, C23; 122.6, C7; 123.2, C6; 124.7, C15; 125.3, C18; 135.6, C9; 142.6, C4; 143.7, C19; 145.5, C11; 148.9, C20; 149.6, C12; 151.0, C2.

#### 3.2.2. H<sub>2</sub>L<sup>2</sup>

2-(1H-benzimidazol-2-yl)-4-bromo-6-methoxyphenol. Following filtration of the H<sub>2</sub>L<sup>1</sup> precipitate, the filtrate was refluxed for 8 h and left to cool down overnight. The resulting off-white microcrystalline precipitate was filtered off, washed with ethanol and diethyl ether. Yield: 1.4 g (44%). Anal. Calc. for C14H11BrN2O2 (319.16): C, 52.7; H, 3.5; N, 8.8. Found: C, 52.6; H, 3.3; N, 8.6%. Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3361, 1491, 1480, 1463, 1443, 1399, 1385, 1248, 1050, 825, 734, 708, 601, Mass spectrum: (EI):  $m/z = 318 (100), [H_2L^2]^+$ . <sup>1</sup>H NMR, dmso-d6: 3.84 (3 H, s. OCH3, H16): 7.20 (1 H, d, *I* = 2.0 Hz, CH, H15): 7.34 (2 H, m, CH, H6, H7); 7.35 (1 H, m, CH, H8); 7.70 (1 H, m, CH, H5); 7.86 (1 H, d, *J* = 2.0 Hz, CH, H13); 13.29 (1 H, s, OH, H11); 13.41 (1 H, s, NH, H1). <sup>13</sup>C NMR: 56.3, C16; 109.9, C14; 111.8, C8; 113.8, C5; 116.5, C13; 118.3, C10; 119.7, C15; 122.8, C7; 123.7, C6; 137.9, C4, C9; 147.8, C11; 149.9, C12; 150.7, C2. Recrystallization from chloroform yielded off-white X-ray quality crystals.

#### 3.2.3. $H_2L^3$

2-(1H-benzimidazol-2-yl)-6-methoxyphenol. A solution of o-phenylenediamine (1.08 g, 0.01 mol) and o-vanillin (3.04 g, 0.02 mol) in ethanol (80 mL) was refluxed for 20 h and left to cool down overnight. The resulting off-white microcrystalline precipitate was filtered off, washed with ethanol and diethyl ether. Yield: 1.25 g (52%). Anal. Calc. C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (240.26): C, 70.0; H, 5.0; N, 11.7. Found: C, 69.6; H, 4.8; N, 11.6%. Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3331, 1495, 1475, 1462, 1449, 1421, 1388, 1253, 1236, 1058, 831, 787, 739, 715, 602. Mass spectrum: (EI): *m*/*z* = 318 (100), [H<sub>2</sub>L<sup>3</sup>]<sup>+</sup>. <sup>1</sup>H NMR, dmso-d6: 3.84 (3 H, s, OCH<sub>3</sub>, H16); 6.96 (1 H, t, *J* = 2.0 Hz, CH, H14); 7.10 (1 H, d, *J* = 2.0 Hz, CH, H13); 7.30 (2 H, m, CH, H6, H7); 7.65 (2 H, m, CH, H5, H8); 7.64 (1 H, d, / = 2.0 Hz, CH, H15); 13.29 (1 H, s, OH, H11); 13.41 (1 H, s, NH, H1). <sup>13</sup>C NMR: 56.2, C16; 111.8, C5, C8; 113.0 C10; 114.4, C13; 118.0, C14; 119.5, C15; 123.3, C6, C7; 142.1, C4, C9; 148.8, C11; 149.0, C12; 152.4, C2.

#### 3.3. Complexes

#### 3.3.1. $[(HL^2)_2Cu], 1$

A mixture of  $H_2L^2$  (0.32 g, 0.001 mol) and  $Cu(CH_3COO)_2 \cdot H_2O$  (0.10 g, 0.0005 mol) in methanol (10 mL) was stirred for 1 h, and the magenta precipitate was filtered off and washed with methanol and diethyl ether. Yield: 0.32 g (91%). *Anal.* Calc.  $C_{28}H_{20}Br_2Cu-N_4O_4$  (699.84): C, 48.1; H, 2.9; N, 8.0. Found: C, 48.4; H, 2.7; N, 8.1%. Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3236, 1537, 1489, 1471, 1459, 1384, 1254, 1229, 1196, 1183, 1069, 841, 799, 747, 738, 711, 625. Slow evaporation of a DMF solution of the precipitate yielded brown crystals of X-ray quality.

#### 3.3.2. $[(HL^3)_2Cu] \cdot H_2O$ , **2**

This complex, prepared in a way similar to that used for **1**, was obtained as a maroon precipitate. Yield: 0.29 g (91%). *Anal.* Calc.  $C_{28}H_{22}CuN_4O_4$  (560.07): C, 60.0; H, 4.3; N, 10.0. Found: C, 59.5; H, 4.1; N, 9.7%. Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3236, 1536, 1489, 1473, 1451, 1436, 1260, 1236, 1200, 1067, 1033, 853, 736, 731, 723.

#### 3.3.3. $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , **3**

This dinuclear complex was prepared according to the experimental procedure reported for the parent Cu–Eu compound [18]. Yield: 0.098 g (58%). *Anal.* Calc.  $C_{48}H_{40}Br_4CuGdN_9O_{17}$  (1555.31): C, 37.1; H, 2.6; N, 8.1. Found: C, 36.8; H, 2.6; N, 8.1%. Characteristic IR absorptions (KBr, cm<sup>-1</sup>): 3360, 1478, 1384, 1279, 1237, 812, 743. Slow diffusion of diethyl ether in an acetonitrile solution of the powder complex yielded X-ray quality green crystals of  $3 \cdot (H_2O) \cdot (C_2H_5OH) \cdot (C_4H_{10}O)$ .

#### 3.3.4. $[(HL^3)_2CuGd(NO_3)_3] \cdot 2(H_2O), 4 \cdot 2(H_2O)$

A mixture of  $H_2L^3Cu \cdot H_2O$  (0.15 g,  $2.7 \times 10^{-4}$  mol) and  $Gd(NO_3)_3 \cdot 5H_2O$  (0.13 g,  $2.7 \times 10^{-4}$  mol) in acetone (10 mL) was stirred for thirty minutes, yielding a bronze precipitate that was filtered off, washed with acetone and diethyl ether and dried. Yield: 0.15 g (62%). *Anal.* Calc.  $C_{28}H_{26}CuGdN_7O_{15}$  (921.35): C, 36.5; H, 2.8; N, 10.6. Found: C, 36.1; H, 2.7; N, 10.1%. Characteristic IR absorptions (KBr): 3217, 1493, 1481, 1452, 1440, 1286, 1247, 1203, 1053, 995, 760, 748, 739 cm<sup>-1</sup>. Slow diffusion of diethyl ether in a 1:1 acetonitrile/ethanol solution of the powder complex yielded X-ray quality reddish-green crystals of **4**-solvent.

#### 3.3.5. $[(HL^3)_2CuTb(NO_3)_3] \cdot 2(H_2O), 5 \cdot 2(H_2O)$

Yield: 0.14 g (56%). *Anal.* Calc.  $C_{28}H_{26}CuTbN_7O_{15}$  (923.03): C, 36.4; H, 2.8; N, 10.6. Found: C, 36.1; H, 2.7; N, 10.1%. Characteristic IR absorptions (KBr): 3206, 1492, 1481, 1451, 1439, 1285, 1246, 1201, 1053, 995, 849, 759, 732 cm<sup>-1</sup>. Slow diffusion of diethyl ether in a 1:1 acetonitrile/ethanol solution of the powder complex yielded X-ray quality reddish-green crystals of **5**-solvent.

Alternately, compounds **4** and **5** may be prepared through one pot reactions: in the first step,  $H_2L^3$  and  $Cu(CH_3COO)_2.H_2O$  are dissolved in a 1:1 acetonitrile/ethanol mixture under stirring and refluxed for 30 min. In the second step, the appropriate lanthanide nitrate, dissolved in the minimum amount of ethanol, is poured into the reaction mixture, which is further refluxed for 2 h. Upon cooling down, compound **4** (**5**) precipitates.

#### 3.4. Physical measurements

C, H, and N elemental analyses were carried out on a Perkin-Elmer 2400 series II device at the microanalytical Laboratory of the Laboratoire de Chimie de Coordination in Toulouse, France. Infrared spectra were recorded at room temperature using a 9800 FTIR spectrometer (Perkin-Elmer) with samples as KBr pellets (%T). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature (295 K) with a Bruker WM250 spectrometer. 2D <sup>1</sup>H COSY experiments using standard programs and 2D pulse-field gradient HMQC <sup>1</sup>H-<sup>13</sup>C correlation using the PFG-HMQC standard program were performed on a Bruker AMX400 spectrometer. All chemical shifts (<sup>1</sup>H and <sup>13</sup>C) are given in ppm versus TMS using dmso d6 as solvent. Mass spectra (EI) were recorded on a Nermag R10-10 spectrometer using acetone as solvent. Magnetic susceptibilities were measured in the 2-300 K temperature range, at a sweeping rate of 2 K min<sup>-1</sup> under an applied magnetic field of 0.1 T, and isothermal magnetization measurements were performed up to 5 T at 2 K, using an MPMS5 Quantum Design SQUID susceptometer. The apparatus was calibrated with palladium metal. All samples were 3 mm diameter pellets molded from ground crystalline samples. Diamagnetic corrections were applied by using Pascal's constants [19]. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [20]. Least-squares fittings were accomplished with an adapted version of the functionminimization program MINUIT [21].

# 3.5. Crystallographic data collection and structure determination for $H_2L^2$ , $[(HL^2)_2Cu]$ , **1**, $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , **3**, $[(HL^3)_2CuGd(NO_3)_3]$ , **4**, and $[(HL^3)_2CuTb(NO_3)_3]$ , **5**

Crystals of  $H_2L^2$ , **1**, **3**, **4**, and **5** were kept in the mother liquor until they were dipped into oil. The selected crystals, sticked on a Mitegen micromount and quickly cooled down to 180 K, were mounted on a Stoe Imaging Plate Diffractometer System (IPDS) (H<sub>2</sub>L<sup>2</sup>, off-white,  $0.40 \times 0.20 \times 0.05$  mm<sup>3</sup>; **1**, brown,  $0.15 \times 0.1 \times$ 0.1 mm<sup>3</sup>; **4**, reddish-green,  $0.25 \times 0.25 \times 0.2$  mm<sup>3</sup>; **5**, reddishgreen,  $0.3 \times 0.25 \times 0.125 \text{ mm}^3$ ) or an Oxford-Diffraction XCALIBUR (**3**, green,  $0.22 \times 0.20 \times 0.18 \text{ mm}^3$ ) using a graphite monochromator ( $\lambda = 0.71073$  Å) and equipped with an Oxford Cryosystems cooler device, and a Cryojet cooler device from Oxford Instruments, respectively. The data were collected at 180 K. The unit cell determination and data integration were carried out using the Xred [22] and CrysAlis RED [23] packages for the data recorded on the IPDS and Xcalibur diffractometers, respectively. 9776 reflections were collected for H<sub>2</sub>L<sup>2</sup>, of which 4504 were independent ( $R_{int} = 0.071$ ), 15040 reflections for **1**, of which 5549 were independent ( $R_{int} = 0.3036$ ), 68765 reflections for **3**, of which 20213 were independent ( $R_{int} = 0.057$ ), 21685 reflections for **4**, of which 7952 were independent ( $R_{int} = 0.1088$ ) and 21687 reflections for **5**, of which 8020 were independent ( $R_{int} = 0.0767$ ). Absorption corrections were applied using Multiscan for H<sub>2</sub>L<sup>2</sup> and complexes 1 and 3 [24]. The structures have been solved by Direct Methods using SIR92 [25a] and SIR97 [25b], and refined by least-squares procedures on  $F^2$  using the program SHELXL97 [26] included in the software package WinGX version 1.63 [27] for 1, 4, and 5, and with the program CRYSTALS [28] for  $H_2L^2$  and 3. The Atomic Scattering Factors were taken from International tables for X-ray crystallography [29]. Hydrogens atoms were introduced in idealized positions and refined by using a riding model. Non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used. Although several data sets were recorded on selected crystals of 1, we could get only 1058 independent reflections with  $I > 2\sigma(I)$  over the 5549 independent ones: therefore, among non-hydrogen atoms, only the copper center and the nitrogen and oxygen donor atoms were anisotropically refined in order to get reliable information about the coordination sphere in spite of the poor refinement. Although better than those recorded for **1**, the relatively low quality of all data sets recorded on selected crystals of 4 and 5 precluded obtaining good enough refinements. In both crystals, the unit cell contains a certain amount of water molecules. However, these water molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the squeeze function of PLATON [30] was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed from the final refinement. Due to the omission of the water molecules from the model, it was not possible to analyse the hydrogen-bonding interactions. There is one cavity of 820 A<sup>3</sup> per unit cell of 5. PLATON estimated that the cavity contains 41 electrons which may correspond to roughly four water molecules within the cell. This is contradictory with the size of the cavity in which we could expect to introduce roughly 41 water molecules. It is well known that the source procedure is very dependent on the low-angle reflections and that the electron count may be underestimated if those reflections are missing which could be the case when data are collected on a CCD type machine. The data for complex 4 were of very poor quality resulting in rather high R and  $wR_2$  values and large residual electron density. Crystal data collection and refinement parameters are summarized in Table 1. Drawings of molecules are performed with the program DIAMOND [31] and 30% probability displacement ellipsoids for non-hydrogen atoms.

	$H_2L^2$	<b>1</b> ∙dmf	$3 \cdot \mathbf{H}_2 \mathbf{O} \cdot \mathbf{EtOH} \cdot (\mathbf{Et})_2 \mathbf{O}$	4	5
Formula	$C_{14}H_{11}BrN_2O_2$	C31H27Br2CuN5O5	C54H56Br4CuGdN9O20	C28H20CuGd N7O13	C28H22CuTbN7O13
F <sub>w</sub>	319.16	772.94	1691.5	883.30	886.99
Temperature (K)	180(2)	180(2)	180(2)	180(2)	180(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	$P2_1/c$	ΡĪ	ΡĪ
a (Å)	7.2960(15)	11.150(5)	16.267(5)	11.475(5)	11.463(5)
b (Å)	11.990(2)	11.211(5)	21.911(8)	12.987(5)	13.032(5)
c (Á)	14.599(3)	13.914(5)	21.231(8)	15.332(5)	15.365(5)
α (°)	75.97(3)	113.526(5)	90	98.744(5)	99.016(5)
β(°)	89.81(2)	104.907(5)	92.454(3)	102.940(5)	102.931(5)
γ (°)	86.92(3)	94.783(5)	90	93.618(5)	93.547(5)
V (Å <sup>-3</sup> )	1237.2(5)	1506.7(11)	7560(5)	2189.7(15)	2198.2(15)
Ζ	4	2	4	2	2
$ ho_{ m calc} ( m g  m cm^{-3})$	1.711	1.704	1.486	1.340	1.340
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.321	3.427	3.331	2.044	2.136
F(0 0 0)	638	774	3332	868	874
Theta range for data collection (°)	1.98-25.98	2.49-26.16	2.67-29.08	2.02-25.95	2.28-26.03
Goodness-of-fit	1.046 (F)	$0.646 (F^2)$	$1.129 (F^2)$	$1.059 (F^2)$	$0.848 (F^2)$
$R_1, wR_2 [I > 2\sigma(I)]$	0.0812, 0.0940	0.0653, 0.1195	0.0875*, 0.0993*	0.0867, 0.2504	0.0469, 0.1072
$R_1$ , w $R_2$ (all data)	0.1148, 0.1195	0.3058, 0.2073	0.1720, 0.1197	0.1278, 0.2635	0.0779, 0.1209

**Table 1** Crystallographic data for  $H_2L^2$  and complexes **1**, **3**, **4** and **5**.

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR_{2} = [\Sigma w (|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \Sigma w |F_{o}^{2}|^{2}]^{1/2}.$ 

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, data see Appendix 1.

#### 4. Results

#### 4.1. Syntheses

The reaction of *o*-phenylenediamine with 5-bromo-2-hydroxy-3-methoxybenzaldehyde in ethanol has been previously described [18]. Following the same experimental procedure, we successively obtained the Schiff base and the *N*-substituted benzimidazole ligand  $H_2L^1$ . Once this ligand was isolated by filtration, the resulting filtrate was refluxed for 8 h, yielding a new precipitate. This off-white solid was identified as the N–H benzimidazole ligand  $H_2L^2$  depicted in Scheme 1. A 2D NMR study (COSY, HMQC) of  $H_2L^1$  and  $H_2L^2$  allowed a straightforward assignment of the entire set of <sup>1</sup>H and <sup>13</sup>C signals, thanks to long range C…H correlations. A similar reaction involving *o*-vanillin and *o*-phenylenediamine yielded the non substituted benzimidazole ligand exclusively.

The monomeric copper complexes  $[(HL^2)_2Cu]$ , **1**, and  $[(HL^3)_2Cu]$ ·H<sub>2</sub>O, **2**, were obtained by reacting H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>3</sup> with copper acetate in methanol, two ligands chelating the copper ion in a head to tail arrangement, as shown by the structural determination of **1**. Cu–Ln complexes (Ln = Gd, Tb) have been obtained from H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>3</sup>, the H<sub>2</sub>L<sup>2</sup> ligand yielding only the copper complex **2**. Complex **3**,  $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , is analogous to the previously reported Cu–Ln complexes of H<sub>2</sub>L<sup>1</sup> (Ln = Eu, Tb, Er, Yb) [18]. Complexes **4**,  $[(HL^3)_2CuGd(NO_3)_3]$ , and **5**,  $[(HL^3)_2CuTb (NO_3)_3]$ , were obtained either through reaction of the mononuclear copper precursor **1** with the appropriate Ln nitrate, or through one pot reactions involving H<sub>2</sub>L<sup>3</sup>, copper acetate and the appropriate Ln nitrate.

#### 4.2. X-ray single crystal structure of $H_2L^2$

The ligand  $H_2L^2$  crystallizes with two independent molecules in the asymmetric unit; they are shown together with an additional molecule in Fig. 1, and selected geometric parameters are collated

in the legend to the figure. In both molecules, the fused benzene and imidazole rings are nearly planar. The dihedral angles between the benzimidazole moiety and the substituted aryl ring are nearly equal for the two independent molecules,  $4.9(3)^{\circ}$  and  $4.4(3)^{\circ}$ , respectively. The N1C7C8C9 (N3C21C22C23) and N2C7C8C13 (N4C21C22C27) torsion angles are almost similar,  $5.4(2)^{\circ}$  ( $4.8(2)^{\circ}$ ) and  $3.6(2)^{\circ}$  ( $3.0(2)^{\circ}$ ), respectively: the molecule is slightly twisted about the C7–C8 (C21–C22) bonds.

Although the phenolic hydrogen atom H(O1) could not be located, intra-molecular N···H–O hydrogen contacts involving the imine and phenol functions (N2···O1 = 2.567(9) Å, N4···O3 = 2.555(12) Å) operate inside both independent molecules: together with the intermolecular contacts described below, they may be responsible for the reduced twist angles reported above. Several weak intermolecular hydrogen contacts connect alternate independent H<sub>2</sub>L<sup>2</sup> molecules into chains developing along *c* (N1···O3, N1···O4, C9···O4, N3···O1', N3···O2' and C23···O2', Fig. 1). Additional weak hydrogen contacts and van der Waals interactions interconnect these chains into the 3D crystal structure of H<sub>2</sub>L<sup>2</sup>.

#### 4.3. X-ray single crystal structure of [(HL<sup>2</sup>)<sub>2</sub>Cu]·dmf, **1**·dmf

Although, for the reasons explained in the experimental section, the refinement achieved for 1 was average, it is of good enough quality to reliably evidence the molecular composition and main geometrical features of the  $[(HL^2)_2Cu]$  complex molecule of **1**. This is important in order to evaluate the changes in the relative arrangement of the HL<sup>2</sup> ligands around the copper center on going from the mononuclear precursor **1** to the dinuclear Cu-Ln complexes 4 and 5. The structure of 1 is shown in Fig. 2 and selected geometric parameters are collated in the legend to the figure. Two  $HL^2$  ligands chelate the copper ion through their imidazolyl nitrogen and phenoxo oxygen atoms, in a relative arrangement close to head to tail. The copper cation adopts a distorted fourcoordinate environment. The dihedral angle of 43.1(5)° between the two coordinating ligands (as defined by the Cu-N-O planes) denotes a substantial distortion from a square planar geometry (0°) towards a tetrahedral geometry (90°). This distortion is confirmed by the values of the angles N1CuN3 and O1CuO3 which deviate largely from 180°: 153.6(5) and 145.2(5)°, respectively.

<sup>\*</sup>  $[I > 3\sigma(I)].$ 



**Fig. 1.** DIAMOND plot of three molecules of H<sub>2</sub>L<sup>2</sup>. Thermal ellipsoids are drawn at the 30% probability level. Except those involved in donor---acceptor contacts, H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): 01–C13 1.358(10), 02–C12 1.368(10), Br1–C10 1.890(9), C7–C8 1.458(11), N1–C1 1.379(11), N1–C7 1.375(10), N2–C6 1.393(10), N2–C7 1.340(11), 03–C27 1.359(10), 04–C26 1.373(10), Br2–C24 1.889(9), C21–C22 1.458(11), N3–C15 1.380(11), N3–C21 1.372(10), N4–C20 1.405(11), N4–C21 1.317(10); C1–N1–C7 106.7(7), C6–N2–C7 105.9(7), C7–C8–C13 118.4(7), C12–O2–C14 116.8(7), C15–N3–C21 107.1(7), C20–N4–C21 105.8(7), C21–C22 - C27 119.1(7), C26–O4–C28 116.3(6); hydrogen contacts N1-··O3 3.243, H1···O3 2.61, N1–H1···O3 132; N1···O4 3.290(12), H1···O4 2.46, N1–H1···O4 162; C9···O4 3.544, H6···O4 2.69, C9–H6···O4 153; N3···O1′ 3.206(12), H31···O1′ 2.53, N3–H31···O1′ 136; N3···O2′ 3.456, H31···O2′ 2.64, N3–H31···O2′ 159; C23···O2′ 3.498, H36···O2′ 2.63, C23–H36···O2′ 156; O3···N4″ 2.555(12), H38···N4″ 1.84, O3–H38···N4 142. Symmetry operations: ′ = *x*, *y*, *z* – 1; ″ = *x*, *y*, 1 + *z*.



**Fig. 2.** DIAMOND plot of  $[(HL^2)_2Cu]$ , **1**. Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu-N1 1.913(14), Cu-O1 1.901(11), Cu-N3 1.899(13), Cu-O3 1.941(13), N1-Cu-O1 92.3(5), O1-Cu-N3 95.6(5), N3-Cu-O3 93.1(5), O3-Cu-N1 94.7(5), N1-Cu-N3 153.6(5), O1-Cu-O3 145.2(5).

The angle of  $65.7(3)^{\circ}$  between the (HL<sup>2</sup>)Cu planes indicates that they are almost perpendicular to each other. The dihedral angles between the benzimidazole moieties and the substituted aryl rings are now considerably larger than in the free ligand,  $8.6(4)^{\circ}$ (16.5(5)°) versus  $4.9(3)^{\circ}$  (4.4(3)°).

The  $[(HL^2)_2Cu]$  molecules of **1** are interconnected through N2H2...O3, N2H2...O4, N4H4...O1 and N4H4...O2 contacts into chains developing along *c* as shown in Fig. 3. The chains of this 1D structure are stacked along *a* and *b* through van der Vaals interactions.

#### 4.4. X-ray single crystal structure of [(HL<sup>1</sup>)<sub>2</sub>Cu(CH<sub>3</sub>CN)<sub>2</sub>Gd(NO<sub>3</sub>)<sub>3</sub>], **3**

The structure of the asymmetric unit of **3**, together with atom labeling scheme is displayed in Fig. 4 and selected geometric parameters are collated in the legend to the figure. The crystal belongs to the monoclinic system,  $P2_1/c$  space group. The molecular structure of **3** is similar to those of the previously reported Cu–Ln complexes of  $H_2L^1$  (Ln = Eu, Tb, Er, Yb) [18]. The copper ion is in a pseudo-octahedral coordination environment including two imidazolyl nitrogen and two phenoxo oxygen atoms provided by two HL<sup>1</sup> ligands and two apical nitrogen atoms from acetonitrile molecules. The phenoxo oxygen donors bridge the metal ions with a Cu…Gd separation of 3.460(3) Å. The equatorial  $N_2O_2$  donor set deviates from planarity: the dihedral angle between the CuN2O3 and CuN4O7 intra-ligand planes is 19.9(4)°. The copper cation is very close (0.02 Å) to the mean N<sub>2</sub>O<sub>2</sub> plane. The gadolinium cation is surrounded by ten oxygen donors, six of them being provided by three bidentate nitrate anions and the remaining four by the  $\{(HL^1)_2Cu\}$  constituting unit. The dihedral angle between the CuO3O7 and GdO3O7 planes is minute:  $0.4(4)^{\circ}\!.$  The overall structure has a  $C_2$  axis running through O(14)-Gd-Cu. Two among the four Br substituents are disordered: they were satisfactorily modeled over two sites with occupancy ratios of 0.5.

## 4.5. X-ray single crystal structures of $[(HL^3)_2CuGd(NO_3)_3]$ , **4**, and $[(HL^3)_2CuTb(NO_3)_3]$ , **5**

X-ray crystallographic studies have shown that **4** and **5** are isostructural, for which reason we describe only  $[(HL^3)_2CuTb(NO_3)_3]$ , **5**. A perspective view of this dinuclear molecule with the corresponding labeling scheme is depicted in Fig. 5 while selected bond distances and angles are listed in the legend to the figure. Two HL<sup>3</sup> ligands sandwich one Cu<sup>2+</sup> ion through their N,O sites and one Tb<sup>3+</sup> ion through their O<sub>2</sub> site, implying a relative arrangement close to head to head, at variance with the relative arrangement close to



**Fig. 3.** DIAMOND plot showing one chain (fragment of 5 molecules) of  $[(HL^2)_2Cu]$ , **1**, developing along *c*. Interatomic N···O distances (Å) characterizing the relevant contacts: N2(H2)···O3, 3.069(18); N2(H2)···O4, 2.844(19); N4(H4)···O1, 3.147(17); N4(H4)···O2, 2.950(19).



**Fig. 4.** DIAMOND plot of  $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , **3.** Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu-N2 1.949(11), Cu-N4 1.977(12), Cu-O3 1.954(9), Cu-O7 1.930(10), Cu-N5 2.64(2), 2.554(14), Gd-O3 2.370(9), 2.610(8), Gd-O7 2.362(10), Gd-O8 2.607(9), Gd-O9 2.465(10), Gd-O10 2.480(10), Gd-O12 2.519(14), Gd-O13 2.470(13), Gd-O15 2.483(12), Gd-O16 2.457(11), Cu-..Gd 3.460(3), N2-Cu-O3 89.6(4), O3-Cu-O7 82.0(3), O7-Cu-N4 91.3(5), N4-Cu-N2 100.6(4), N2-Cu-O7 162.5(5), N4-Cu-O3 163.6(5), N5-Cu-N6 176.0(5), N5-Cu-N2 83.8(5), N5-Cu-N4 99.1(5), N5-Cu-O3 94.7(5), N5-Cu-O7 81.6(5), N6-Cu-N2 97.0(5), N6-Cu-N4 84.6(5), N6-Cu-O3 81.4(4), N6-Cu-O7 97.0(4), O3-Gd-O7 65.2(3), O3-Gd-O9 79.4(3), O3-Gd-O12 147.2(4), O4-Gd-O3 62.5(3), O4-Gd-O7 114.3(3), O4-Gd-O8 176.7(3), O7-Gd-O8 62.6(3), O7-Gd-O9 92.6(3), O7-Gd-O10 130.8(3), O9-Gd-O10 51.7(3), O12-Gd-O13 50.0(4), O15-Gd-O16 51.0(4).

head to tail of their  $HL^2$  analogs in the mononuclear copper precursor,  $[(HL^2)_2Cu]$ . The dihedral angles between the benzimidazolyl groups and the aryl rings are also considerably larger than that in the free ligand  $H_2L^2$  (9.7(3)° (23.6(3)°) versus 4.9(3)° (4.4(3)°)). The Cu<sup>2+</sup> ion has square-planar geometry; however, N1, O1, O3 and N3 deviate significantly from their mean plane: the angle between the CuO3N3 and CuN1O1 planes is 26.1(2)°. The terbium ion is ten-coordinate. In addition to the four oxygen atoms from the  $\{(HL^3)_2Cu\}$  constituting unit, six oxygen atoms from three bidentate nitrato anions complete its coordination sphere. The two metal ions are doubly bridged to one another through two phenoxo oxygen atoms belonging to the  $HL^3$  ligand with a Cu…Tb separation of 3.458(2) Å. The dihedral angle between the O1TbO3 and O1CuO3 planes equals  $0.8(2)^\circ$ .



Fig. 5. DIAMOND plot of  $[(HL^3)_2CuTb(NO_3)_3]$ , 5. The thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Cu-N1 = 1.925(5), Cu-N3 = 1.934(5), Cu-O1 = 1.934(4), Cu-O3 = 1.914(4), Tb-O1 = 2.337(4),Tb-O2 = 2.687(4), Tb-O3 = 2.361(4). Tb-O4 = 2.609(4). Tb-O5 = 2.448(5), Tb-06 = 2.465(5). Tb-08 = 2.470(5). Tb-O9 = 2.479(4), Tb-O11 = 2.468(5), Tb-O12 = 2.471(5), Cu...Tb = 3.458(2), N1-Cu-O1 = 92.10(18), O1-Cu-O3 = 80.67(16), O3-Cu-N3 = 91.80(19), N3-Cu-N1 = 101.5(2), 01-Cu-N3 = 159.3(2), N1-Cu-O3 = 157.6(2), Cu-O1-Tb 107.75(17), Cu-O3-Tb 107.53(17), O1-Tb-O2 61.51(13), O1-Tb-O3 = 64.05(14), O1-Tb-O4 118.41(13), O1-Tb-O5 80.85(16), O1-Tb-O8 153.26(18), O1-Tb-O9 130.85(15), 02-Tb-O4 179.64(16), 05-Tb-O6 52.02(15), 06-Tb-O8 74.91(19), 09-Tb-O4 110.71(15), 09-Tb-011 72.48(17), 012-Tb-05 164.47(15), 012-Tb-06 130 48(16)

#### 4.6. Magnetic properties

The magnetic susceptibilities of the Cu<sup>II</sup> precursor **1** and Cu–Ln complexes **3–5** have been measured in the 2–300 K temperature range in an applied magnetic field of 0.1 T. The thermal variation of the  $\chi_M T$  product for complexes **1**,  $[(HL^2)_2Cu]$ , and **4**,  $[(HL^3)_2CuGd(NO_3)_3]$ , are shown in Figs. 6 and 7, respectively,  $\chi_M$  being the molar magnetic susceptibility corrected for the diamagnetism of the ligands. At 50 K, the  $\chi_M T$  product for complex **1** equals 0.37 cm<sup>3</sup> mol<sup>-1</sup> K, which is very close to the value expected for an isolated Cu<sup>II</sup> ion (0.374 cm<sup>3</sup> mol<sup>-1</sup> K for g = 2. The  $\chi_M T$  product remains practically constant down to 12 K (0.36 cm<sup>3</sup> mol<sup>-1</sup> K) and then decreases to 0.21 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. Considering the 1D chains formed through the N2H2...O3, N2H2...O4, N4H4...O1 and N4H4...O2 contacts, we fitted the magnetic data by consider-



**Fig. 6.** Thermal variation of the magnetic susceptibility,  $\chi_M$ , and  $\chi_M T$  product for complex **1**, [(HL<sup>2</sup>)<sub>2</sub>Cu]. The solid line corresponds to the best fit of the experimental data (see text).

ing chain interactions. As shown in Fig. 6, the fits obtained when computing the magnetic susceptibility with the assumption of an Heisenberg chain of *S* = 1/2 spins [32] were fairly good for the parameter values *g* = 2.03, *J* (cm<sup>-1</sup>) = -0.76, Par (paramagnetic contribution) = 0.0%, with an agreement factor  $R = \sum [(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2 / \sum [(\chi_M T)_{obs}]^2 = 2.3 \times 10^{-4}$ .

At 300 K, the  $\chi_M T$  product for complex **4** equals 8.27 cm<sup>3</sup> mol<sup>-1</sup> K, which is very close to the value expected for one copper and one gadolinium ions without magnetic interactions (8.25 cm<sup>3</sup> mol<sup>-1</sup> K). Lowering the temperature results initially in a smooth increase of  $\chi_M T$  (8.51 cm<sup>3</sup> mol<sup>-1</sup> K at 100 K) and then in a steeper increase, up to 9.73 cm<sup>3</sup> mol<sup>-1</sup> K at 8 K, followed by a smooth decrease to 9.70 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K (Fig. 7). The maximum value compares well with that expected for an *S* = 4 spin-state resulting from ferromagnetic interaction between Gd (*S* = 7/2) and Cu (*S* = 1/2) centers with  $g_{Cu} = g_{Gd} = 2$ . Similar experimental data have been obtained for complex **3**, [(HL<sup>1</sup>)<sub>2</sub>Cu(CH<sub>3</sub>CN)<sub>2</sub>-Gd(NO<sub>3</sub>)<sub>3</sub>] (Fig. S1).

A quantitative analysis has been performed on the basis of an expression derived from the spin-only Hamiltonian  $H = -J_{CuGd}$  ( $S_{Cu}S_{Cd}$ ). Least squares fitting to the experimental data obtained for **4** leads to  $J_{CuGd} = 6.5(2) \text{ cm}^{-1}$ , g = 1.99(1) with a good agreement factor,  $R = 1 \times 10^{-4}$  ( $R = \sum [(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2 / \sum [(\chi_M T)_{obs}]^2$ ). In order to take into account the slight  $\chi_M T$  decrease at very low temperature, a Weiss constant  $\theta$  has been introduced in the theoretical expression, leading to the minute -0.006 K value (Fig. 7).



**Fig. 7.** Thermal variation of the magnetic susceptibility,  $\chi_M$ , and  $\chi_M T$  product for complex **4**,  $[(HL^3)_2CuGd(NO_3)_3] \cdot 2(H_2O)$ . The solid line corresponds to the best fit of the experimental data (see text).



**Fig. 8.** Thermal variation of the magnetic susceptibility,  $\chi_M$ , and  $\chi_M T$  product for complex **5**,  $[(HL^3)_2CuTb(NO_3)_3] \cdot 2(H_2O)$ .

A quantitative analysis performed for complex **3**,  $[(HL^1)_2Cu(CH_3CN)_2Gd(NO_3)_3]$ , on the basis of the same spin-only Hamiltonian leads to very similar parameter values,  $J_{CuGd} = 7.2(2) \text{ cm}^{-1}$ , g = 2.01(2) and  $R = 1 \times 10^{-4}$  (Fig. S1).

Although a quantitative analysis of complex **5**,  $[(HL^3)_2CuTb (NO_3)_3]$ , is not possible, due to the orbital momentum of the terbium ion [33,34], its magnetic behavior is shown in Fig. 8. At 300 K, the  $\chi_M T$  product equals 12.2 cm<sup>3</sup> mol<sup>-1</sup> K, as expected for non interacting copper and terbium ions. Upon lowering the temperature,  $\chi_M T$  decreases steadily to 10.3 cm<sup>3</sup> mol<sup>-1</sup> K at 20 K before reaching a value of 9.3 cm<sup>3</sup> mol<sup>-1</sup> K at 3 K. The decrease of  $\chi_M T$  with temperature in the high temperature range is most probably governed by depopulation of the Tb Stark levels, precluding obtaining reliable information on the presence and sign of the Cu–Tb interaction, these two magnetic phenomena being competitive.

#### 5. Discussion

The unsubstituted parent ligand of  $H_2L^2$  and  $H_2L^3$ , 2-(1*H*-benzimidazol-2-yl)phenol [35,36], and substituted derivatives [37], have been previously described. To the best of our knowledge however, the synthetic route to  $H_2L^2$  and  $H_2L^3$ , is novel as compared to that used in the previous reports [35–37] (condensation between salicylic acid (or its substituted derivatives) and o-phenylenediamine). These organic molecules have been studied as laser dyes [38-40], while their coordination chemistry has been studied in conjunction with the electro- [41] and photoluminescence [42] properties of their complexes. The Fe<sup>III</sup> chemistry of this type of ligand has also been explored owing to the interest of their mononuclear and dinuclear oxo (hydroxo) bridged Fe<sup>III</sup> complexes as models of non-heme iron metalloproteins with mono and dinuclear active sites [38,43,44]. However to date, the potential dinucleating ability of their 6-methoxy(phenol) derivatives has not been explored.

In previous work [33,45], we have described several examples of strictly dinuclear Cu–Gd complexes that exhibit ferromagnetic behavior. Once we know that the Cu-Gd interaction is ferromagnetic in a large majority of simple dinuclear complexes, it is interesting to link these units in order to aim at high-spin entities. In this contribution, we have considered ligands including simultaneously one 6-methoxyphenol and one benzimidazole moieties in view of the potential dinucleating and bridging abilities offered by their 6-methoxyphenol and imidazole parts, respectively. Indeed, the bridging ability of such ligands may result from deprotonation of their benzimidazole ring to yield an imidazolate bridge. A look at the molecular structure of the Cu-Ln complexes 4 and 5 shows that the mean planes of the two HL<sup>3</sup> ligands are far from being aligned. Deprotonation of the benzimidazole functions would release two supplementary coordination sites: their involvement as bridges between dinuclear Cu-Ln units would significantly modify the relative arrangement of the two ligands. Unfortunately, attempts to further deprotonate (HL<sup>2</sup>)<sup>-</sup> and (HL<sup>3</sup>)<sup>-</sup> did not yield the desired products: we could not isolate crystals from the ill-defined powder compounds obtained. However, the magnetic data collected on samples of these compounds indicate that the ferromagnetic Cu-Gd interaction is lost. We have observed that Ln complexation implies a rearrangement of the two  $(HL^2)^-$  or  $(HL^3)^-$  ligands chelated to the copper ion, cf. the molecular structures of **4** and **5** versus that of **1**. It is then guite plausible that the presence of an additional nitrogen donor at each ligand is able to promote a novel rearrangement: indeed benzimidazole type ligands are good chelating ligands toward Ln ions [46,47].

In the two structurally characterized Cu–Gd complexes **3** and **4**, the dihedral angle defined by the OCuO and OGdO planes is close to  $0^{\circ}$  (0.4(4) and 0.3(4)°), respectively) and magnetic interactions

of 7.2 and 6.5 cm<sup>-1</sup> have been found, respectively. We have previously shown that a correlation between the interaction parameter *I* and the above mentioned dihedral angle does exist: lowering the bending of the CuO<sub>2</sub>Gd core causes an increase of the ferromagnetic interaction [3]. The J values obtained for complexes 3 and 4 do not seem to agree with our previous data: J values around 10 cm<sup>-1</sup> would be expected. A closer look at the molecular structures of **3** and **4** evidences the main difference. In the present examples the central CuO<sub>2</sub>Gd core is the only part of the structure to be planar: the two independent (HL<sup>3</sup>)<sup>–</sup> ligands linked to the Cu and Gd ions depart to a large extent from planarity. This situation is at variance with the previous examples where the Cu and Gd ions were coordinated to a unique ligand and where the deformations were located at the CuO<sub>2</sub>Gd core. It becomes clear that the dihedral angle is not the right parameter to gauge the interaction value, here. But it is clear that the orbitals of the bridging phenoxo oxygen atoms are not correctly oriented to yield the larger interaction, thus explaining that *J* values lower than 10 cm<sup>-1</sup> are obtained for complexes 3 and 4.

#### 6. Conclusion

We have shown that benzimidazole ligands 2-substituted by phenyl rings bearing phenol and methoxy functions can yield heterodinuclear Cu-Ln complexes. These 2-(2'-hydroxy-3'-methoxyphenyl)benzimidazole derivatives coordinate copper ions in a head to tail arrangement while introduction of a lanthanide ion induces a rearrangement of the ligands in head to head relative positions, allowing formation of a new  $O_2O_2$  coordination site available for the incoming Ln ion. This situation has been encountered for bidentate 1-NH and 1-N substituted benzimidazole ligands. The Cu-Gd interactions are ferromagnetic, as observed in a large majority of Cu-Gd complexes. Nevertheless, these new complexes are complementary to the previous ones for the Cu-O<sub>2</sub>-Gd core is kept planar while deformations are borne by the ligands, at variance with previous examples in which the constraints were located at the Cu–O<sub>2</sub>–Gd core. The main difference originates from the presence of two independent ligands in the coordination spheres conferring a degree of freedom greater than that allowed by a unique tetradentate ligand. Consequently, at variance with our previous suggestion, the strength of the magnetic interaction is not related solely to the dihedral angle between the CuOO and GdOO planes in the central core. Furthermore, these benzimidazole ligands do possess an NH function not involved in the coordination sites of the heterodinuclear complex: through deprotonation, heterodinuclear units like 4 and 5 are thus good candidates for selfassembling into larger entities that should be high-spin species. We have not yet reached this goal for the behavior of these heterodinuclear units, upon deprotonation, is more complex than expected, each bidentate benzimidazole ligand being able to promote a novel rearrangement. By using a unique ligand including both benzimidazole moieties, we expect better results: work in this direction is in progress.

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#### Appendix A. Supplementary data

CCDC 767999, 768000, 768001, 768002 and 768003 contain the supplementary crystallographic data for the ligand  $H_2L^2$  and complexes **1**, **3**, **4**, and **5**, respectively. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2010.04.010.

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