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# Synthesis, crystal structures and magnetic characterization of heterodinuclear Cu<sup>II</sup>Gd<sup>III</sup> and Cu<sup>II</sup>Tb<sup>III</sup> Schiff base complexes

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#### ABSTRACT

Preparation, crystal structures and magnetic properties of new heterodinuclear Cu<sup>II</sup>Gd<sup>III</sup> (1) and Cu<sup>II</sup>Tb<sup>III</sup> (2) complexes [CuLn(L)(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>MeOH]NO<sub>3</sub>:MeOH (where Ln = Gd, Tb) with the hexadentate Schiffbase compartmental ligand *N*,*N'*-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (H<sub>2</sub>L =  $C_{19}H_{20}N_2O_4Br_2$ ) (0) have been described. Crystal structure analysis of 1 and 2 revealed that they are isostructural and form discrete dinuclear units with dihedral angle between the O1Cu1O2 and O1Gd1/Tb1O2 planes equal to 2.5(1)° and 2.6(1)°, respectively. The variable-temperature and variable-field magnetic measurements indicate that the metal centers in 1 and 2 are ferromagnetically coupled (*J* = 7.89 cm<sup>-1</sup> for 1). Crystal and molecular structure of the Schiff base ligand (0) has been also reported. The complex formation changes the conformation of Schiff base ligand molecule.

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# 1. Introduction

The heteronuclear **3d-4f** complexes attract much attention due to their interesting magnetic properties, as well as, for investigating the nature of magnetic exchange interactions between lanthanide and transition metal atoms and their exploitable applications. They are used as magnets, high-temperature superconductors, molecular sensors or luminescent materials [1-16]. The most of reported 3d-4f complexes have been derived from bicompartmental Schiff-base ligands having an inner site with N<sub>2</sub>O<sub>2</sub> chelating centers binding **3d** cations (radii 0.75–0.6 Å) and outer O<sub>2</sub>O<sub>2</sub> coordination site which is larger than the inner one and able to accommodate greater, oxophilic, 4f lanthanide ions (radii 1.06-0.85 Å) [1,3,6,14–34]. A search in the literature revealed that the architectural study on 3d-4f compounds has been well developed but little is known about the exchange coupling parameter  $(J_{Ln-M})$ [1,10,18-30]. The paramagnetic rare earth ions Ln(III) (except of Gd(III)) are characterized by an anisotropic magnetic moment leading to difficulty in analyzing J<sub>Ln-M</sub> [1,4–6,14,35–38]. The magnetic research of polynuclear Cu-Gd compounds came to the conclusion that the exchange interaction within the Cu-Gd ions is in most cases ferromagnetic [3,14–21,24,30,39–43] but Costes et al. reported examples of complexes in which this interaction is antiferromagnetic [42,43]. Moreover the geometrical factors have been found to influence the nature of exchange coupling

\* Corresponding author. E-mail address: beata.cristovao@poczta.umcs.lublin.pl (B. Cristóvão). [2,16,24,26,42,43]. In comparison to the studies of Cu-Gd heteronuclear systems [1-4,9,12,14-21,24,26,27,39-43] the magnetic properties of Cu-Tb coordination compounds have been much less investigated [1,35,44-50]. We have undertaken study on heteronuclear **3d–4f** complexes in order to investigate the influence of the structural parameters on the nature and magnitudes of the exchange interactions and gain more information on the magnetic properties of Cu(II)-Ln(III) compounds. In our study we have synthesized new heterodinuclear Cu<sup>II</sup>Gd<sup>III</sup> (1) and Cu<sup>II</sup>Tb<sup>III</sup> (2) compounds [CuLn(L)(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>MeOH]NO<sub>3</sub>·MeOH, by using the hexadentate Schiff base compartmental ligand N,N'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine. We determined crystal structures of the free ligand and complexes, measured their magnetic susceptibilities in the temperature range of 1.8-300 K as well as measuring the variation of the magnetization (M) at 2 K as a function of the field (H) up to 5 T.

## 2. Experimental

#### 2.1. Materials

All chemicals and solvents used for the synthesis were of commercially available reagent grade and were used without further purification.

The Schiff base ligand *N*,*N*-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine ( $H_2L = C_{19}H_{18}Br_2N_2O_4$ ) (**0**) has been synthesized by the 2:1 condensation of 5-bromo-2-hydroxy-3methoxybenzaldehyde and 1,3-diaminopropane in methanol



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according to the reported procedure [11,24]. The Schiff base was separated as yellow needles and recrystallized twice from methanol. The compound is stable at room temperature and has been characterized by elemental analysis, FTIR spectroscopy and single crystal X-ray structural analysis. *Anal.* Calc. for  $C_{19}H_{18}Br_2N_2O_4$ : C, 45.61; H, 4.00; N, 5.60. Found: C, 45.32; H, 3.76; N, 5.67%.

#### 2.2. Synthesis of the complexes

Compounds 1 and 2 were obtained in a similar way. For instance, to prepare 1, a mixture of Schiff base ligand H<sub>2</sub>L (0.4 mmol, 0.1999 g) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.4 mmol, 0.0799 g) in methanol (30 ml) was vigorous stirred for 30 min at room temperature. Then, a methanol solution of Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.2 mmol, 0.0903 g) was added dropwise, and the mixture was kept stirring for another 30 min at ambient temperature. The solution was filtered to remove the suspended materials and kept in the low temperature for very slow evaporation. After a few days green crystals suitable for X-ray diffraction were appeared which were collected by filtration, washed with cold methanol and dried. Terbium(III) nitrate was prepared from Tb<sub>4</sub>O<sub>7</sub> (0.05 mmol, 0.0374 g) with nitric acid. Anal. Calc. for C<sub>21</sub>H<sub>32</sub>N<sub>5</sub>O<sub>18</sub>Br<sub>2</sub>CuGd (1023.12) (1): C, 24.64; H, 3.13; N, 6.84; Cu, 6.21; Gd, 15.38. Found: C, 25.04; H, 2.87; N, 6.83; Cu, 6.43; Gd, 15.62%. Anal. Calc. for C<sub>21</sub>H<sub>32</sub>N<sub>5</sub>O<sub>18</sub>Br<sub>2</sub>CuTb (1024.80) (2): C, 24.61; H, 3.13; N, 6.84; Cu, 6.21; Tb, 15.52. Found: C, 24.19; H, 2.94; N, 6.84; Cu, 6.46; Tb, 15.71%.

#### 2.3. Physical measurements

The contents of carbon, hydrogen and nitrogen in the analyzed compounds were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser.

The contents of copper and lanthanides were established using ED XRF spectrophotometer (Canberra-Packard).

The FTIR spectra of complexes were recorded over the range of  $4000-200 \text{ cm}^{-1}$  using M-80 spectrophotometer (Carl Zeiss Jena). Samples for IR spectra measurements were prepared as KBr discs.

The magnetization of the Cu<sup>II</sup>Gd<sup>III</sup> (**1**) and Cu<sup>II</sup>Tb<sup>III</sup> (**2**) powdered samples was measured over the temperature range of 1.8–300 K using a Quantum Design SQUID – based MPMSXL-5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements sample of compounds were made at magnetic field 0.5 T. The SQUID magnetometer was calibrated with the palladium rod sample. Corrections are based on subtracting the sample – holder signal and contribution  $\chi_D$  estimated from the Pascal's constants [51] and equal  $420 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> for Cu<sup>II</sup>Gd<sup>III</sup> (**1**) and  $408 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> for Cu<sup>II</sup>Tb<sup>III</sup> (**2**), respectively and the temperature independent paramagnetism of the Cu<sup>2+</sup> centers equal  $+60 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>.

#### 2.4. Single crystal X-ray analysis

The crystallographic measurements were performed on an Oxford Diffraction Xcalibur CCD diffractometer with the graphitemonochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at the temperature of 100(2) K. Data sets were collected using the  $\omega$  scan technique, with an angular scan width of 1.0°. The programs cRYSALIS CCD and cRYSALIS RED [52] were used for data collection, cell refinement and data reduction. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied for **1** and in case of **2** and **0** – the analytical absorption correction based on the indexing of the crystal faces [53]. The structures were solved by direct methods using SHELXS-97 and refined by the full-matrix least-squares on  $F^2$  using the SHELXL-97 [54] (both operating under WINGX [55]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The C9 and C10 atoms are disordered in structures **1** and **2** into two almost equally occupied positions (sof's = 0.584(6):0.416(6) in **1** and 0.606(6):0.394(6) in **2**), whereas atom C8 was treated as unaffected by disorder. The coordinates of C10/C10A and C8/C8A in **1** and C10/C10A and C9/C9A in **2** were refined with the same anisotropic displacement parameters (constrains were applied with EADP instruction). Hydrogen atoms from water and methanol molecules were found in difference Fourier map and refined isotropically. Distances O–H in water molecules were restrained in **2** by DFIX instruction to 0.8 Å with an estimated standard deviation 0.05. All remaining H-atoms were positioned geometrically and allowed to ride on their parent atoms, with  $U_{iso}(H) = 1.2/1.5 U_{eq}(C)$ . A summary of the conditions for the data collection and the structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP3 for Windows [56], Mercury [57] and Diamond [58].

#### 3. Results and discussion

#### 3.1. Infrared spectra

The FTIR spectrum of the Schiff base ligand,  $H_{2}L(\mathbf{0})$  shows strong absorption band at 1636 cm<sup>-1</sup> which is characteristic for the azomethine v(C=N) group. In the spectra of the complexes 1 and **2** this band is shifted to lower wavenumbers and appears at 1628 cm<sup>-1</sup> indicating the participation of the azomethine nitrogen in coordination to metal [1,59-64]. A strong band observed at 1252 cm<sup>-1</sup> in free Schiff base spectrum has been assigned to phenolic v(C–O) stretching vibration. On complexation, this band appears at lower frequency 1240 cm<sup>-1</sup>, confirming the involvement of the phenolic oxygen in the metal-ligand bonding. [60,63,64]. This is in accord with the X-ray structural data. The structural determination of **1** and **2** (see below) show that, the Schiff base acts as hexadentate chelating ligand coordinated to metal ions through two nitrogen and four oxygen atoms. The strong band at  $1384 \text{ cm}^{-1}$  is present only in the spectra of the complexes and can be assigned to vibrations of the nitrate group  $v(NO_3)$ [1,59,65]. In the FTIR spectra of the 1 and 2 the broad medium bands with the maximum around 3430 cm<sup>-1</sup> may be attributed to the OH stretching vibrations of water molecules, v(O-H)[1,59,60]. On the basis of crystal structures of these compounds we know that the water molecules are present in the complexes and they are bonded to the lanthanide(III) ions. The occurrence of two bands at *ca*. 572 and 448  $cm^{-1}$  respectively, which are not seen in the spectrum of the free Schiff base ligand, gives further evidence for M-O and M-N interaction. The selected FTIR bands of the free Schiff base ligand **0** and compounds **1** and **2** are listed in Supporting Information, Table S1.

#### 3.2. Crystal structure description

# 3.2.1. Description of crystal and molecular structure of the free Schiff base ligand **0**

A search of the Cambridge Structural Database (CSD, Version 5.32 with updates November 2010 and February 2011 [70] revealed only six crystal structures with N,N'-bis(5-bromo-2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane (**0**) as a ligand (*Refcodes:* FOBBEE, FOBBII, TEHROO, WAQDEX, XUJRIE and XUJ-ROK). However, there is no crystal structure deposition of the free ligand in the CSD. Here, we report the crystal structure of **0** in 100 K (Table 1). The atomic numbering scheme is shown in Fig. 1. The single crystal X-ray analysis confirmed the molecular structure of ligand **0** with favoured enolimine over ketonamine form (Table 2). The complex formation changes the conformation of ligand molecule mainly through the bending of propylene-1,3diamine bridge and rotation of aromatic rings (Table 2). In the solid



Fig. 1. Molecular structure of  ${\bf 0}$  with atomic labels. The displacement ellipsoids were drawn at the 50% probability level.

state the molecule of **0** has bent conformation with dihedral angle between two rings being 83°, while in **1** and **2** these angles are equal to 26°. Both hydroxyl O1/O2 atoms form intramolecular hydrogen bonds to N1/N2 atoms. The adjacent molecules interact through weak C-H...O/N, C-H... $\pi$ , and C-H...Br interactions (Table 3).

#### 3.2.2. Description of the structure of 1 and 2

The elemental analyses and infrared spectral data for the Cu<sup>II</sup>–Gd<sup>III</sup> (**1**) and Cu<sup>II</sup>–Tb<sup>III</sup> (**2**) coordination compounds are consistent with the crystal structures determined by single crystal X-ray diffraction (Table 1). The title compounds [CuLn(C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>) (NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>MeOH]NO<sub>3</sub>·MeOH (where Ln = Gd, Tb) are isostructural with very small lattice distortion index eA = 0.00024 [66]. The isostructurality indices calculated for **1** and **2** with Löwdin orthogonalization indicate very close similarity between these two crystal structures ( $\Pi$  = 0.0025;  $I_i$ (50) = 96.6%;  $I_v^{max}$  = 99.6%) [67].

Crystals of **1** and **2** are composed of discrete dinuclear cations with a salen-type Schiff base ligands. In the asymmetric unit there are additionally one uncoordinated nitrate anion and one methanol molecule. The propylene bridge of organic ligand in both complexes is disordered over two almost equally occupied positions. A view of these units including the atomic numbering scheme is illustrated in Figs. 2 and 3. The central part of the coordination core in **1** and **2** is occupied by Cu(II) and Gd(III)/Tb(III) ions. The metal ions are bridged via two phenolic oxygen atoms from organic ligand. The inner salen-type cavity is occupied by Cu(II) ion. Lanthanide ions are present in the open, larger space of the compartmental ligand. The M–O(phenolate) bond distances for copper(II) and gadolinium(III)/terbium(III) ions are in accordance with the values reported for related **3d–4f** coordination compounds (Table 2) [28,35,69]. The CuOOGd/Tb core including two phenoxo oxygen atoms is essentially planar with the largest deviation from mean plane being 0.021 and 0.022 Å for Cu ion in **1** and **2**, respectively. The dihedral angle between the Cu10102 and Gd1/ Tb10102 planes is equal to 2.5(1)° in **1** and 2.6(1)° in **2**. The Cu1– Gd1/Tb1 distances are quite short: 3.539(1) and 3.522(4) Å, in **1** and **2**, respectively.

The coordination polyhedron of the lanthanide cation has a shape resembling distorted tricapped trigonal prism (Fig. 4). It is formed by four O atoms of the polydentate Schiff base ligand, two  $\eta^2$  chelating O atoms from a nitrate anion, and three O atoms from aqua ligands. The lanthanide-oxygen bond lengths depend on the chemical nature of the O atoms (methoxy, nitrate, aqua or phenoxo). They vary from 2.358(3) Å for Tb–O(aqua) to 2.537(2) Å for Gd–O(methoxy) (Table 2). These values are similar to the bond lengths reported earlier [15,21,24]. In the title complexes the copper is surrounded by six donor atoms. The equatorial N<sub>2</sub>O<sub>2</sub> donors from the Schiff base ligand are nearly planar with the largest deviation from the mean plane being 0.189 Å for O1 atom in 1 and 0.197 Å for atom O2 in 2. Additionally, two oxygen atoms: one from methanol molecule and one from monodentate nitrate ion, are coordinated to the apical position of the Cu(II) center - resulting in an octahedral coordination environment. The crystal structures of these two novel complexes are stabilized by strong intermolecular hydrogen bonds (Table 3) between aqua, nitrate and methanol molecules. In the crystal lattice the adjacent molecules are held together by classical intermolecular hydrogen bonds involving the coordinated water molecules and noncoordinated O atoms of the monodentate nitrate ligand (Table 3). The uncoordinated nitrate ion and methanol molecule are also connected by hydrogen bond. The molecules form layers perpendicular

Table 1

Crystallographic data, details of data collection and structure refinement parameters for the Schiff base ligand (H<sub>2</sub>L) 0 and compounds 1 and 2.

Crystal data	0	1	2
Empirical formula	$C_{19}H_{20}Br_2N_2O_4$	$C_{21}H_{32}Br_2CuGdN_5O_{18}$	C <sub>21</sub> H <sub>32</sub> Br <sub>2</sub> CuTbN <sub>5</sub> O <sub>18</sub>
Formula weight	500.19	1023.12	1024.80
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	ΡĪ	$P2_1/n$	$P2_1/n$
a (Å)	4.592(1)	9.978(2)	9.955(1)
b (Å)	14.682(1)	16.753(2)	16.720(1)
<i>c</i> (Å)	15.694(1)	19.921(3)	19.859(1)
α (°)	113.88(1)	90	90
β (°)	93.39(1)	90.22(3)	90.20(1)
γ (°)	96.70(1)	90	90
$V(Å^3)$	954.3(1)	3330.0(9)	3305.5(1)
Ζ	2	4	4
Crystal form/color	plate/yellow	block/green	block/green
Crystal size (mm)	$0.40 \times 0.30 \times 0.15$	$0.46 \times 0.32 \times 0.27$	$0.42 \times 0.40 \times 0.32$
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.741	2.041	2.059
$\mu$ (mm <sup>-1</sup> )	4.275	5.096	5.267
Absorption correction	analytical	multi-scan	analytical
$\theta$ range (°)	2.62-25.24	2.59–28.28	2.64-28.28
Reflections collected	5980	27961	15076
Independent reflections (R <sub>int</sub> )	3459 (0.0297)	8182 (0.0267)	8188 (0.0248)
Reflections observed $(I > 2\sigma(I))$	2769	6872	6680
Data/restrains/parameters	3459/0/244	8182/0/480	8188/6/468
Goodness-of-fit (GOF) on $F^2$	1.052	0.978	0.999
$R_1, wR_2 [I > 2\sigma(I)]$	0.0540, 0.1544	0.0210, 0.0470	0.0339, 0.0811
$R_1$ , $wR_2$ (all data)	0.0631, 0.1574	0.0276, 0.0477	0.0418, 0.0824
$\Delta ho_{ m max}$ , $\Delta ho_{ m min}$ (e Å $^{-3}$ )	1.84, -0.75	1.40, -0.75	2.47, -1.94

Table	2
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Selected geometric parameters (Å,  $^\circ)$  in the coordination environments of the metal center.

0			
Bond lengths			
N1-C7	1.277(1)	N2-C11	1.276(1)
01-C1	1.344(8)	02–C12	1.345(7)
Torsions			
C7-N1-C8-C9	-109.0(6)	C9-C10-N2-C11	108.3(6)
N1-C8-C9-C10	166.7(4)	C9-C10-N2-C11	108.3(6)
C8-C9-C10-N2	-176.2(4)	C10-N2-C11-C17	-175.4(5)
1			
Bond lengths			
Gd1-01	2.387(2)	Gd1-07	2.382(2)
Gd1-02	2.398(1)	Cu1-N1	1.997(2)
Gd1-03	2.537(2)	Cu1-N2	1.969(2)
Gd1-04	2.513(2)	Cu1-01	1.955(1)
Gd1-08	2.483(2)	Cu1-02	1.993(2)
Gd1-09	2.510(2)	Cu1-011	2.532(2)
Gd1-05	2.369(2)	Cu1-017	2.509(2)
Gd1-06	2.387(2)	Cu1–Gd1	3.539(1)
Angles			
Cu1-01-Gd1	108.81(6)	01-Gd1-03	63.69(5)
Cu1-02-Gd1	107.06(6)	02-Gd1-04	64.71(5)
01-Gd1-02	64.06(5)	α	2.5(1)
Torsions			
N1-C8-C9-C10	60.8(6)	C8-C9-C10-N2	-82.3(7)
$\alpha$ – dihedral angle between the Cu10	0102 and Gd10102 planes.		
2			
Bond lengths			
Tb1-01	2.372(2)	Tb1-07	2.361(3)
Tb1-02	2.378(2)	Cu1-N1	1.989(3)
Tb1-03	2.528(2)	Cu1-N2	1.961(3)
Tb1-04	2.502(2)	Cu1-01	1.951(2)
Tb1-08	2.461(2)	Cu1-02	1.995(2)
Tb1-09	2.494(3)	Cu1-011	2.537(3)
Tb1-05	2.358(3)	Cu1-017	2.501(3)
Tb1-06	2.377(3)	Cu1-Tb1	3.522(4)
Angles			
Cu1-O1-Tb1	108.74(9)	O1-Tb1-O3	63.81(7)
Cu1-O2-Tb1	106.95(9)	O2-Tb1-O4	64.81(8)
01-Tb1-02	64.42(8)	α	2.6(1)
Torsions			
N1-C8-C9-C10	61.3(8)	C8-C9-C10-N2	-81.0(9)

 $\alpha$  – dihedral angle between the Cu10102 and Tb10102 planes.



Fig. 2. Molecular structure of 1 with atomic labels. The displacement ellipsoids were drawn at the 50% probability level.



Fig. 3. Molecular structure of  ${\bf 2}$  with atomic labels. The displacement ellipsoids were drawn at the 50% probability level.

#### Table 3

Hydrogen bonding geometry.

001-H1N10.841.862.671(6)1.46.8(.3)02-H200200.932.633.457.8(.6)1.44.4(.3)0.94.040200.992.633.397(.9)1.31.6(.3)0.94.040200.992.953.699.7)12.22.3)1.84.1803 <sup>(H)</sup> 0.982.443.1937(.7)13.30.3)1.84.1803 <sup>(H)</sup> 0.982.663.1621.631.84.1803 <sup>(H)</sup> 0.982.663.1621.631.84.1803 <sup>(H)</sup> 0.982.663.1621.631.84.1803 <sup>(H)</sup> 0.982.663.1621.631.84.1803 <sup>(H)</sup> 0.78(.3)1.99(.3)2.657(.3)1.694.6(0.5-1580110.78(.3)1.99(.3)2.757(.3)1.694.6(0.5-1580130.78(.3)2.543(.3)3.371(.3)1.71.480.5-1580140.77(.3)2.08(.3)2.761(.3)1.77.760.7-17780170.99(.4)2.687(.3)1.71.48(.3)1.62.46(.5)0.7-17780170.99(.3)2.58(.3)2.693(.3)1.71.48(.5)0.7-1778016 <sup>(H)</sup> 0.89(.3)2.84(.3)1.71.78(.5)0.7-1778016 <sup>(H)</sup> 0.89(.3)2.58(.3)3.247(.3)1.62.46(.5)0.7-1778016 <sup>(H)</sup> 0.932.543(.3)3.243(.3)1.620.7-1778016 <sup>(H)</sup> 0.932.543(.3)3.243(.3)1.61.26(.5)0.7-1778016 <sup>(H)</sup> 0.932.58(.3)3.247(.3)1.62.46(.5)0.7-1778016 <sup>(H)</sup> 0.932.543(.3)3.247(.1) <t< th=""><th>D–HA</th><th>D–H (Å)</th><th>HA (Å)</th><th>DA (Å)</th><th>D–HA (°)</th></t<>	D–HA	D–H (Å)	HA (Å)	DA (Å)	D–HA (°)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0				
$02+128.$ $0.24$ $0.84$ $1.83$ $2.57(6)$ $146.8(2)$ $02+188.$ $0.87$ $0.38$ $0.67$ $3.367(9)$ $13.16(3)$ $02+180.$ $0.87$ $0.88$ $0.67$ $3.367(9)$ $13.2(3)$ $18+18803^{(10)}$ $0.98$ $2.44$ $3.193(7)$ $13.0(3)$ $18+18803^{(10)}$ $0.98$ $2.50$ $3.445$ $148$ $19+19C02^{(10)}$ $0.98$ $2.50$ $3.445$ $148$ $19+19C02^{(10)}$ $0.98$ $2.50$ $3.445$ $168$ $29$ -centroid between atoms C12, C13. $19.3(3)$ $19.3(3)$ $19.3(3)$ $19.3(3)$ $05-158013$ $0.78(3)$ $2.54(3)$ $3.77(3)$ $19.4(6)$ $05-1458013$ $0.78(3)$ $2.54(3)$ $3.71(3)$ $15.7(6)$ $05-1458013$ $0.78(3)$ $2.54(3)$ $3.71(3)$ $15.7(6)$ $07-1478017$ $0.99(4)$ $2.08(4)$ $2.847(3)$ $17.18(8)$ $06-1468013^{(10)}$ $0.72(3)$ $2.08(3)$ $2.76(3)$ $17.17(8)$ $07-1478012^{(10)}$ $0.77(3)$ $19.3(3)$ $2.63(3)$ $17.17(8)$ $07-1478012^{(10)}$ $0.77(3)$ $2.58(3)$ $3.207(3)$ $168.7(6)$ $07-1478016^{(10)}$ $0.80(3)$ $2.58(3)$ $3.424(3)$ $168.7(6)$ $07-1478015^{(10)}$ $0.80(3)$ $2.58(3)$ $3.424(3)$ $16.12(6)$ $07-1478015^{(10)}$ $0.80(3)$ $2.58(3)$ $3.424(3)$ $16.12(6)$ $07-1478015^{(10)}$ $0.80(3)$ $2.58(3)$ $3.20$	01-H1N1	0.84	1.86	2.601(6)	146.4(3)
$(9-198, .03^{10})$ 0.992.633.465(8)144.(3) $(18-118.A., N2^{10})$ 0.992.953.597(9)13.163) $(18-118.A., 03^{10})$ 0.982.503.445148 $(19-119, 02^{10})$ 0.982.563.162163Symmetry codes: $(1) - x, - y, - z;$ $(ii) - 1 - x, - y, - z;$ $(iv) - 1 + x, y, z;$ og 1 - centroid between atoms C1, C2; cg 2 - centroid between atoms C1, C2; cg 2 - centroid between atoms C1, C2; cg 2 - centroid between atoms C1, C3; cg 2 - centroid between atoms C1, C4; cg 2 -	02–H2…N2	0.84	1.83	2.576(6)	146.8(3)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C9–H9BO3 <sup>(i)</sup>	0.99	2.63	3.485(8)	144.4(3)
	C18–H18A…N2 <sup>(i)</sup>	0.98	2.67	3.397(9)	131.6(3)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C9–H9ABr2 <sup>(ii)</sup>	0.99	2.95	3.659(7)	129.2(3)
$\begin{array}{c} (13-1182.cq) (19) & 0.08 & 2.50 & 3.445 & 148 \\ (19-1192.cq) (10) & 0.08 & 2.66 & 3.162 & 163 \\ Symmetry codes; (1) - x, - y, - z; (ii) - x, - y, - z; (ii) - 1 + x, - y, - z; (iv) - 1 + x, y, z; cg1 - centroid between atoms C1, C2; cg2 - centroid between atoms $	C18–H18AO3 <sup>(iii)</sup>	0.98	2.44	3.193(7)	133.0(3)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	C18–H18Bcg1 <sup>(iv)</sup>	0.98	2.50	3.445	148
	C19–H19Ccg2 <sup>(iv)</sup>	0.98	2.66	3.162	163
1         0           05-H58011         0.81(3)         1.99(3)         2.577(3)         168.9(6)           05-H58013         0.78(3)         2.54(3)         3.148(3)         155.5(6)           05-H58013         0.78(3)         2.62(3)         3.371(3)         162.8(6)           07-H78017         0.99(4)         2.08(4)         2.847(3)         171.8(6)           06-H68014         0.72(3)         2.08(3)         2.761(3)         157.7(6)           07-H78017         0.99(4)         2.08(4)         2.847(3)         171.8(6)           06-H68014         0.72(3)         2.08(3)         2.761(3)         157.7(6)           07-H78017         0.98(3)         2.01(3)         2.785(2)         162.5(6)           017-H17016 <sup>(iii)</sup> 0.80(3)         2.05(3)         3.207(3)         136.1(6)           017-H17015 <sup>(iii)</sup> 0.80(3)         2.65(3)         3.424(3)         161.2(6)           C3-H58013         0.05 <sup>(i)</sup> 2.97         2.41         3.332(3)         163.2(6)           017-H17015 <sup>(ii)</sup> 0.80(3)         2.65(3)         3.424(3)         164.2(6)         164.2(6)           C3-H58013         0.97         2.41         3.332(4)	Symmetry codes: (i) $-x$ , $-y$ , $-z$ ; (ii) $-x$ ,	-y, 1-z; (iii) $-1-x, -y, -z;$	(iv) -1 + x, y, z; cg1 - centroid	between atoms C1, C2; cg2 - co	entroid between atoms C12, C13.
05-H5A018         0.81(3)         1.86(3)         2.657(3)         168.9(6)           05-H5B011         0.78(3)         1.99(3)         2.757(3)         169.4(6)           05-H5B013         0.78(3)         2.54(3)         3.148(3)         135.5(6)           05-H5B017         0.99(4)         2.08(4)         2.847(3)         171.8(8)           06-H6B014         0.72(3)         2.08(3)         2.751(3)         157.7(6)           07-H7A0120         0.77(3)         1.93(3)         2.663(3)         168.7(6)           018-H1806 <sup>(iii)</sup> 0.74(4)         2.12(4)         2.845(3)         171.7(8)           017-H17015 <sup>(iii)</sup> 0.80(3)         2.58(3)         3.207(3)         168.7(6)           017-H17015 <sup>(iii)</sup> 0.80(3)         2.58(3)         3.244(3)         161.2(6)           017-H17015 <sup>(iii)</sup> 0.80(3)         2.58(3)         3.244(3)         168           017-H17015 <sup>(iii)</sup> 0.80(3)         2.58(3)         3.243(3)         168           017-H17015 <sup>(ii)</sup> 0.93         2.51         3.400(3)         162           05-H58013         0.97         2.34         3.251(1)         158           016-H106015 <sup>(i)</sup> 0.97 <td>1</td> <td></td> <td></td> <td></td> <td></td>	1				
105-107018         0.31(3)         1.86(3)         2.597(3)         168.40           05-H58013         0.78(3)         2.54(3)         3.148(3)         135.5(6)           05-H58014         0.78(3)         2.62(3)         3.371(3)         162.8(6)           07-H78017         0.99(4)         2.08(4)         2.847(3)         171.8(8)           06-H68014         0.72(3)         1.99(3)         2.663(3)         168.7(6)           07-H78012 <sup>(0)</sup> 0.77(3)         1.99(3)         2.663(3)         168.7(6)           07-H7A012 <sup>(0)</sup> 0.77(3)         1.99(3)         2.663(3)         168.7(6)           07-H7A012 <sup>(0)</sup> 0.74(4)         2.12(4)         2.845(3)         171.7(8)           017-H17015 <sup>(0)</sup> 0.80(3)         2.56(3)         3.207(3)         136.1(6)           017-H17015 <sup>(0)</sup> 0.80(3)         2.65(3)         3.242(3)         162           C3-H3015 <sup>(0)</sup> 0.97         2.47         3.347(7)         150           C10-H10A08 <sup>(0)</sup> 0.97         2.49         3.50(3)         172           Symmetry codes: (i) x - 1, y. z; (ii) x + 1, y. z; (iii) 1/2 - x, y + 1/2 - z; (v) 3/2 - x, y - 1/2, 1/2 - z; (v) 1/2 + x, 1/2 - y, 1/2 + y, 1/2 - z; (vii) 1 - x, 1 - y, - z         1 - y, - z </td <td></td> <td>0.01(2)</td> <td>1.86(2)</td> <td>2 (57(2)</td> <td>168.0(6)</td>		0.01(2)	1.86(2)	2 (57(2)	168.0(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.81(3)	1.00(3)	2.057(3)	168.9(6)
03-B3013         0.7403         2.2403         3.1403         133.00           05-B3B013         0.7403         2.2403         3.3713         162.866           07-B3B017         0.99(4)         2.08(4)         2.847(3)         171.8(8)           06-B4BB014         0.72(3)         2.08(3)         2.761(3)         157.7(6)           07-H7A012 <sup>(0)</sup> 0.77(3)         1.93(3)         2.663(3)         168.7(6)           018-H18016 <sup>(0)</sup> 0.74(4)         2.12(4)         2.845(3)         171.7(8)           017-H17015 <sup>(0)</sup> 0.80(3)         2.05(3)         3.424(3)         161.2(6)           017-H17015 <sup>(0)</sup> 0.80(3)         2.58(3)         3.207(3)         156.1(6)           017-H17015 <sup>(0)</sup> 0.80(3)         2.51         3.442(3)         168           C7-H7010 <sup>(0)</sup> 0.93         2.51         3.400(3)         162           C8-H8A015 <sup>(0)</sup> 0.97         2.47         3.347(7)         150           C10-H10A08 <sup>(0)</sup> 0.97         2.69         3.500(4)         147           C19-H1809 <sup>(0)</sup> 0.97         2.69         3.500(4)         147           C19-H19B09 <sup>(0)</sup> 0.96         2.58         3.530(		0.78(3)	1.99(3)	2.757(3)	109.4(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.78(2)	2.34(3)	3.140(3)	153.3(0)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.78(3)	2.02(3)	3.371(3)	171 8(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	07-H/B017	0.99(4)	2.08(4)	2.847(3)	1/1.8(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	00-H0B014	0.72(3)	2.08(3)	2.761(3)	157.7(6)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$07 - H7A012^{(i)}$	0.77(3)	1.93(3)	2.693(3)	1/1.9(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$O_{18}$ U18 $O_{16}$	0.86(3)	1.81(3)	2.003(3)	108.7(0)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	017_U17_01C(iii)	0.74(4)	2.12(4)	2.845(3)	1/1./(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	017-H17016 <sup>(iii)</sup>	0.80(3)	2.01(3)	2.785(2)	102.5(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.80(3)	2.58(3)	3.207(3)	130.1(0)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$OI/-HI/N5^{(m)}$	0.80(3)	2.65(3)	3.424(3)	161.2(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C3 - H3 \dots O12^{(V)}$	0.93	2.41	3.324(3)	168
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C_{1} = H_{1} = O_{1} = O_{1}$	0.93	2.51	3.400(3)	162
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C10 U100 O2(vi)	0.97	2.47	3.347(7)	150
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$C10-H10A08^{(1)}$	0.97	2.34	3.261(11)	158
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C10_H10PO0(vii)	0.97	2.69	3.500(4)	147
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C19-H19809 <sup>(11)</sup>		2.58	3.530(3)	1/2
1 - y, -z.205-H5A0180.74(3)1.91(3)2.653(4)176.3(4)05-H5B0110.77(3)1.99(3)2.743(4)166.4(4)05-H5B0130.77(3)2.54(4)3.146(4)137.3(4)05-H5BN40.77(3)2.61(3)3.356(4)163.5(4)07-H7B0170.79(4)1.95(4)2.729(3)173.6(5)06-H6B0140.74(4)2.04(4)2.751(3)161.9(5)07-H7A012 <sup>(1)</sup> 0.84(4)1.87(4)2.685(4)163.1(4)06-H6A013 <sup>(1)</sup> 0.83(4)1.84(4)2.663(4)168.9(5)018-H18016 <sup>(11)</sup> 0.842.012.843(4)171017-H17015 <sup>(11)</sup> 0.842.623.422(4)160017-H17015 <sup>(111)</sup> 0.842.623.422(4)167017-H17015 <sup>(111)</sup> 0.842.623.422(4)167017-H17015 <sup>(111)</sup> 0.842.623.442(6)150017-H17015 <sup>(111)</sup> 0.952.393.322(4)167C7-H7010 <sup>(10)</sup> 0.952.483.398(4)162C8-H8A015 <sup>(10)</sup> 0.992.453.344(6)150C10-H10A08 <sup>(101)</sup> 0.992.673.404(5)146	Symmetry codes: (1) $x = 1, y, z;$ (1) $x + 1, y = 1, y =$	y, z; (III) $1/2 - x, y + 1/2, 1/2 - 1/2$	2; (IV) 3/2 - x, y - 1/2, 1/2 - 2;	(v) 1/2 + x, 1/2 - y, 1/2 + 2; (v1) 3	2 - x, 1/2 + y, 1/2 - 2; (VII) $1 - x,$
2 $05-H5A018$ $0.74(3)$ $1.91(3)$ $2.653(4)$ $176.3(4)$ $05-H5B011$ $0.77(3)$ $1.99(3)$ $2.743(4)$ $166.4(4)$ $05-H5B013$ $0.77(3)$ $2.54(4)$ $3.146(4)$ $137.3(4)$ $05-H5BN4$ $0.77(3)$ $2.61(3)$ $3.356(4)$ $163.5(4)$ $07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(1)}$ $0.84(4)$ $1.87(4)$ $2.663(4)$ $163.1(4)$ $06-H6A013^{(1)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(iii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $017-H17012^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $167$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C16-H16013^{(vi)}$ $0.99$ $2.29$ $3.230(19)$ $159$	1 - y, -2.				
$05-H5A018$ $0.74(3)$ $1.91(3)$ $2.653(4)$ $176.3(4)$ $05-H5B011$ $0.77(3)$ $1.99(3)$ $2.743(4)$ $166.4(4)$ $05-H5B013$ $0.77(3)$ $2.54(4)$ $3.146(4)$ $137.3(4)$ $05-H5B014$ $0.77(3)$ $2.61(3)$ $3.356(4)$ $163.5(4)$ $07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.663(4)$ $168.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(iii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $017-H17015^{(iii)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $017-H17010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $017-H17010^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $017-H17010^{(v)}$ $0.99$ $2.29$ $3.230(19)$ $159$ $017-H17010^{(v)}$ $0.99$ $2.29$ $3.230(19)$ $146$	2				
$05-H5B011$ $0.77(3)$ $1.99(3)$ $2.743(4)$ $166.4(4)$ $05-H5B013$ $0.77(3)$ $2.54(4)$ $3.146(4)$ $137.3(4)$ $05-H5BN4$ $0.77(3)$ $2.61(3)$ $3.356(4)$ $163.5(4)$ $07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.685(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(iii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.99$ $2.29$ $3.20(19)$ $146$	O5-H5AO18	0.74(3)	1.91(3)	2.653(4)	176.3(4)
$05-H5B013$ $0.77(3)$ $2.54(4)$ $3.146(4)$ $137.3(4)$ $05-H5BN4$ $0.77(3)$ $2.61(3)$ $3.356(4)$ $163.5(4)$ $07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.663(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(vi)}$ $0.99$ $2.29$ $3.230(19)$ $159$ $C16-H1603^{(vi)}$ $0.95$ $2.67$ $3.404(5)$ $146$	O5-H5BO11	0.77(3)	1.99(3)	2.743(4)	166.4(4)
$05-H5BN4$ $0.77(3)$ $2.61(3)$ $3.356(4)$ $163.5(4)$ $07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.685(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $167$ $017-H17015^{(iii)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.95$ $2.67$ $3.201(19)$ $159$	05-H5B013	0.77(3)	2.54(4)	3.146(4)	137.3(4)
$07-H7B017$ $0.79(4)$ $1.95(4)$ $2.729(3)$ $173.6(5)$ $06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.685(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $167$ $017-H17015^{(iii)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C3-H3012^{(iv)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.99$ $2.29$ $3.230(19)$ $159$	O5–H5BN4	0.77(3)	2.61(3)	3.356(4)	163.5(4)
$06-H6B014$ $0.74(4)$ $2.04(4)$ $2.751(3)$ $161.9(5)$ $07-H7A012^{(i)}$ $0.84(4)$ $1.87(4)$ $2.685(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17015^{(iii)}$ $0.84$ $1.95$ $2.782(4)$ $171$ $017-H17015^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17015^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.95$ $2.67$ $3.201(9)$ $146$	07–H7B017	0.79(4)	1.95(4)	2.729(3)	173.6(5)
$07-H7A012^{(1)}$ $0.84(4)$ $1.87(4)$ $2.685(4)$ $163.1(4)$ $06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(iii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $1.95$ $2.782(4)$ $171$ $017-H17015^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H1705^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.95$ $2.67$ $3.200(19)$ $146$	06-H6B014	0.74(4)	2.04(4)	2.751(3)	161.9(5)
$06-H6A013^{(i)}$ $0.83(4)$ $1.84(4)$ $2.663(4)$ $168.9(5)$ $018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $1.95$ $2.782(4)$ $171$ $017-H17015^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H1705^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.95$ $2.67$ $3.201(9)$ $146$	07–H7A012 <sup>(i)</sup>	0.84(4)	1.87(4)	2.685(4)	163.1(4)
$018-H18016^{(ii)}$ $0.84$ $2.01$ $2.843(4)$ $171$ $017-H17016^{(iii)}$ $0.84$ $1.95$ $2.782(4)$ $171$ $017-H17015^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H1705^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.99$ $2.29$ $3.230(19)$ $159$ $C16-H16.013^{(vi)}$ $0.95$ $2.67$ $3.494(5)$ $146$	06–H6A013 <sup>(i)</sup>	0.83(4)	1.84(4)	2.663(4)	168.9(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O18-H18O16 <sup>(ii)</sup>	0.84	2.01	2.843(4)	171
$017-H17015^{(iii)}$ $0.84$ $2.57$ $3.201(4)$ $133$ $017-H17N5^{(iii)}$ $0.84$ $2.62$ $3.422(4)$ $160$ $C3-H3012^{(iv)}$ $0.95$ $2.39$ $3.322(4)$ $167$ $C7-H7010^{(v)}$ $0.95$ $2.48$ $3.398(4)$ $162$ $C8-H8A015^{(v)}$ $0.99$ $2.45$ $3.344(6)$ $150$ $C10-H10A08^{(vi)}$ $0.99$ $2.29$ $3.230(19)$ $159$ $C16-H16013^{(vi)}$ $0.95$ $2.67$ $3.494(5)$ $146$	017-H17016 <sup>(iii)</sup>	0.84	1.95	2.782(4)	171
$017-H17N5^{(iii)}$ 0.842.623.422(4)160 $C3-H3012^{(iv)}$ 0.952.393.322(4)167 $C7-H7010^{(v)}$ 0.952.483.398(4)162 $C8-H8A015^{(v)}$ 0.992.453.344(6)150 $C10-H10A08^{(vi)}$ 0.992.293.230(19)159 $C16-H16013^{(vi)}$ 0.952.673.494(5)146	017-H17015 <sup>(iii)</sup>	0.84	2.57	3.201(4)	133
C3-H3012 <sup>(iv)</sup> 0.952.393.322(4)167C7-H7010 <sup>(iv)</sup> 0.952.483.398(4)162C8-H8A015 <sup>(v)</sup> 0.992.453.344(6)150C10-H10A08 <sup>(vi)</sup> 0.992.293.230(19)159C16-H160.13 <sup>(vi)</sup> 0.952.673.494(5)146	017–H17…N5 <sup>(iii)</sup>	0.84	2.62	3.422(4)	160
$C7-H7010^{(v)}$ 0.952.483.398(4)162 $C8-H8A015^{(v)}$ 0.992.453.344(6)150 $C10-H10A08^{(vi)}$ 0.992.293.230(19)159 $C16-H16013^{(vi)}$ 0.952.673.494(5)146	C3-H3012 <sup>(iv)</sup>	0.95	2.39	3.322(4)	167
C8-H8A015 <sup>(v)</sup> 0.99       2.45       3.344(6)       150         C10-H10A08 <sup>(vi)</sup> 0.99       2.29       3.230(19)       159         C16-H16       0.13 <sup>(vi)</sup> 0.95       2.67       3.494(5)       146	C7-H7010 <sup>(v)</sup>	0.95	2.48	3.398(4)	162
C10-H10A08 <sup>(v1)</sup> 0.99       2.29       3.230(19)       159         C16-H16       013 <sup>(vi)</sup> 0.95       2.67       3.494(5)       146	C8-H8AO15 <sup>(v)</sup>	0.99	2.45	3.344(6)	150
C16-H16 O13 <sup>(vi)</sup> 0.95 2.67 3.494(5) 146	C10-H10AO8 <sup>(vi)</sup>	0.99	2.29	3.230(19)	159
	C16-H16O13 <sup>(vi)</sup>	0.95	2.67	3.494(5)	146
C19–H19B09 <sup>(vn)</sup> 0.98 2.55 3.525(5) 172	C19–H19BO9 <sup>(vii)</sup>	0.98	2.55	3.525(5)	172

Symmetry codes: (i) x - 1, y, z; (ii) x + 1, y, z; (iii) 1/2 - x, y + 1/2, 1/2 - z; (iv) 3/2 - x, y - 1/2, 1/2 - z; (v) 1/2 + x, 1/2 - y, 1/2 + z; (vi) 3/2 - x, 1/2 + y, 1/2 - z; (vii) 1 - x, 1 - y, -z.

to the *c* crystallographic axis (Fig. 5). Between layers in the crystal structure the weak hydrogen bonds C–H...O and additionally intermolecular contacts between O10(nitrate) and Br2 atoms being shorter than sum of van der Waals radii (3.292(3) and 3.287(3) Å for **1** and **2**, respectively) (symmetry code -x + 1, -y + 1, -z) appear. These contacts do not conform to the rules of halogen bond because the C–Br...O angle is *ca* 80°. However, the short Br...O distances may be attributed to anisotropic distribution of electron density around the halogen nucleus [70]. The intermolecular interactions give an extended three-dimensional network but do not lead to short internuclear contacts with the shortest separations between metal ions being observed for Cu…Tb 7.543(4) Å and Cu…Gd 7.557(3) Å.

## 3.3. Magnetic properties

The magnetic properties of  $Cu^{II}Gd^{III}$  (1) were studied over the temperature range of 1.8–300 K. Plots of magnetic susceptibility

 $\chi_{\rm m}^{-1}$  and  $\chi_{\rm m}T$  product versus T are given in Fig. 6. The thermal dependence of  $\chi_m^{-1}$  obeys the Curie–Weiss law in the whole temperature range with  $\theta$  = 1.7 K and C = 8.19 cm<sup>3</sup> mol<sup>-1</sup> K. At 300 K,  $\chi_{\rm m}T$  is equal to 8.16 cm<sup>3</sup> K mol<sup>-1</sup> which roughly corresponds to the value  $(\chi_m T = 8.25 \text{ cm}^3 \text{ K mol}^{-1})$  expected for the two isolated  $Cu^{II}$  (S = 1/2) and Gd<sup>III</sup> (4f<sup>7</sup>, J = 7/2, L = 0, S = 7/2, <sup>8</sup>S<sub>7/2</sub>) ions, with a g value assumed to be equal to 2. When the temperature is lowered,  $\chi_m T$  product remains constant until 120 K and then slightly increases, reaching a maximum of 9.63 cm<sup>3</sup> K mol<sup>-1</sup> at 10 K, and then decreases to 7.80 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The behavior observed in the 300–10 K range is indicative of a ferromagnetic interaction between the Gd<sup>III</sup> and Cu<sup>II</sup> ions. The facts that the maximum  $\chi_m T$  value at 10 K is slightly lower than expected value  $(10 \text{ cm}^3 \text{ mol}^{-1} \text{ K})$  for total spin state *S* = 4, and the  $\chi_m T$  values are decreased at low temperatures may be attributed to zero-field splitting (ZFS) effects of the S = 4 ground state and/or antiferromagnetic interactions between heterobinuclear entities in crystal



**Fig. 4.** A view of coordination polyhedron in **2**. The disordered part of propylene bridge with lower occupation factor was omitted for clarity.

lattice. The Gd<sup>III</sup> with an <sup>8</sup>S<sub>7/2</sub> single-ion ground state does not possess a first-order orbital moment [51]. Thus the contributions of the orbital angular momentum and the anisotropic effect do not need to be taken into consideration. Considering the occurrence of intramolecular magnetic interactions (*J*) and intermolecular interactions (*J*') [9,71] the coupling of the spin momentum of Gd<sup>III</sup> and Cu<sup>II</sup> ions is described by the spin Hamiltonian  $H = -JS_{Cu}S_{Gd} - J'S_{Cu}S_{Gd}$ . Taking into consideration the *g* values associated with the low-lying levels E(4) = 0 and E(3) = 4J,  $g_4 = (7g_{Gd} + g_{Cu})/8$ , and  $g_3 = (9g_{Gd} - g_{Cu})/8$  [72] we obtain the following theoretical expression (1) and (2) [24]:



**Fig. 6.** Temperature dependence of experimental  $\chi_m T$  ( $\bigcirc$ ) and  $\chi_m^{-1}$  ( $\bullet$ ) vs. *T* for complex **1**. The solid lines is the calculated curve derived from Eqs. (1) and (2).

$$F_d = \frac{15g_4^2 + 7g_3^2 \exp(-4J/kT)}{9 + 7 \exp(-4J/kT)}$$
(1)

$$\chi_m T = \frac{4N\beta^2 T F_d}{kT - J' F_d} + N_\alpha T \tag{2}$$

where  $\beta$  is the Bohr magneton, *g* is Lande factor, *k* is Boltzman's constant, and  $N_{\alpha}$  is the temperature-independent paramagnetism. A least-squares fitting of the experimental data between 10 and 200 K (solid line in Fig. 6) leads to  $J = 7.89(1) \text{ cm}^{-1}$ ,  $f' = -0.066(1) \text{ cm}^{-1}$ ,  $g_{Cu} = 2.02(2)$ ,  $g_{Gd} = 1.98(1)$  and  $N_{\alpha} = 2.76 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  with a good agreement factor  $R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2/\Sigma(\chi_{exp}T)^2$  ( $R = 1.10 \times 10^{-4}$ ). This fitting indicates an intradimer Cu–Gd ferromagnetic interaction. The analysis also reveals very weak intermolecular antiferromagnetic interaction propagated through extended networks formed by hydrogen bonds. To confirm the nature of the ground state of **1**, we investigated the variation of the magnetization, *M*, with respect to the field, at 2 K.



Fig. 5. View of molecular layers perpendicular to c crystallographic axis in crystal structure of 2. The hydrogen atoms were omitted for clarity. Dashed lines indicate intermolecular Br...O contacts.



**Fig. 7.** Field dependence of the magnetization for complex **1**. The solid line is the Brillouin function curve for a S = 4 state of Cu<sup>II</sup>–Gd<sup>III</sup> unit; dashed line is the Brillouin function for two independent S = 1/2 and S = 7/2 systems.

Table 4												
The comparison	of the	structural	and	magnetic	data	for	a	series	of	some	Cu <sup>II</sup> Gd <sup>I</sup>	11
complexes.												

Compound	CuGd	$\alpha^{a}$ (°)	J	Refs.
	(Å)		$(cm^{-1})$	
$LCu(Me_2CO)Gd(NO_3)_3$	3.475	12.7	7.3	16
CuLGd(NO <sub>3</sub> ) <sub>3</sub> ]·Me <sub>2</sub> CO	3.428	12.9	7.0	15
$LCu(Me_2CO)Gd(NO_3)_3$	3.427	11.8	5.6	26
$L^2Cu(MeOH)Gd(NO_3)_3$	3.484	12.5	6.8	28
$L^4Cu(OCMe_2)Gd(NO_3)_3$	3.523	16.6	4.8	28
$CuGd(H_2O)(NO_3)(ems)_2$	3.306	24.5	1.88	2
$LCu(O_2COMe)Gd(thd)_2$	3.473	19.1	3.5	14
$[LCu(Me_2CO)Gd(NO_3)_3]_2$	3.375	11	7.4	77
Cu(salabza)Gd(hfac) <sub>3</sub>	3.248	47.4	0.8	79
CuGdLCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> Cl·2H <sub>2</sub> O	3.51	1.7	10.1	78
CuGd(hfa)3(salen)(meim)	3.252	39.6	1.42	30
GdCu(OTf)(bdmap) <sub>2</sub> (H <sub>2</sub> O)THF	3.31	0.6	-0.04	76
$CuL^{1}Gd(NO_{3})_{3}$	3.65	6.1	3.5	44
$CuGdL^{2}(H_{2}O)(NO_{3})_{3}$	3.62	39.1	-0.49	44
$CuGd(hmp)_2(NO_3)_3(H_2O)_2$	3.345	20.5	3.36	80
[CuLGd(L)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> MeOH]NO <sub>3</sub> ·MeOH	3.539	2.52	7.89	this
				work

<sup>a</sup> Dihedral angle between planes OCuO and OGdO.

The results are shown in Fig. 7, where molar magnetization M is expressed in  $\mu_{\rm B}$  units. The saturation magnetization is close to 8  $\mu_{\rm B}$ . The magnetization data have been compared with the sum of the Brillouin functions of isolated Gd<sup>III</sup> and Cu<sup>II</sup>, as well as with the Brillouin function of the S = 4 pair state. The experimental magnetizations of **1** is greater than for two independent S = 1/2 and S = 7/2system and very close with the Brillouin function of S = 4 state. These results confirm the ferromagnetic interaction between Gd<sup>III</sup> and Cu<sup>II</sup> and demonstrating that the low temperature decrease of  $\gamma_m T$  is not due to ZFS effects and there exists antiferromagnetic interactions between neighboring dinuclear units. The complex 1 considered in this work exhibits ferromagnetic  $I_{Cu-Gd}$  interactions, as in the majority of previously published Cu<sup>II</sup>Gd<sup>III</sup> complexes [2,3,8,14,15,21,24,26,28,30,42,68,73-78]. The ferromagnetic character of the magnetic interaction within the GdO<sub>2</sub>Cu systems has been attributed [30,42] to the coupling between the ground and the excited configuration of Gd<sup>III</sup>–Cu<sup>II</sup> in which an electron has been transferred from the singly occupied 3d copper orbital to an empty 5d gadolinium orbital. Given that their largest values would be associated with the gadolinium 5d orbitals oriented along the two



**Fig. 8.** Temperature dependence of experimental  $\chi_m T$  ( $\Box$ ) and  $\chi_m^{-1}$  ( $\blacksquare$ ) vs. *T* for complex **2**.

Gd-O (bridging atom) directions, one concludes easily that the larger the bending network the smaller the value of these parameter J, and consequently, the weaker the ferromagnetic coupling is. In an attempt to find some structural characteristic, which could correlate with the magnetic behavior in the CuO<sub>2</sub>Gd bridging network, we analyzed some the Cu<sup>II</sup>Gd<sup>III</sup> dinuclear complexes reported in the literature [2,3,8,14,15,21,24,28,30,42,68,73-78]. There is some correlation between  $J_{CuGd}$  and the intramolecular Cu...Gd distance and this can be fitted to an exponential function such that - $J = A \exp(Bd_{Cu...Gd})$  where  $A = 6.409 \times 10^4$  and B = -2.833 with J in cm<sup>-1</sup> and Cu...Gd distance between the two metal centers in Å [79]. Using the value of Cu...Gd = 3.539(1) Å as found in the present complex **1**, this relationship leads to a value of  $J_{\text{calc}} = 14.5 \text{ cm}^{-1}$ , which poorly match the experimental value 7.89 cm<sup>-1</sup>. It was also noted that the  $J_{CuGd}$  values and the dihedral angle  $\alpha$  defined by the two O-Cu-O and O-Gd-O planes of the CuO<sub>2</sub>Gd bridging core could be correlated by an exponential function,  $I = A \exp^{-B\alpha}$  with A = 11.5 and B = 0.054 [24]. According to this correlation, *J* should be ca. 10 cm<sup>-1</sup> for 1 ( $\alpha$  = 2.52°). In the obtained complex 1 the interaction is ferromagnetic ( $I = 7.89 \text{ cm}^{-1}$ ) as it is for reported diphenolato-bridged Cu<sup>II</sup>Gd<sup>III</sup> dinuclear complexes which yield / values varying from 1.0 to 10.1 cm<sup>-1</sup> [2,14–16,28,30,42,74–78]. The experimental value of 7.89 cm<sup>-1</sup> is not very different from this hypothesis. The intermolecular shortest metal-metal distance in 1 is large enough to consider the dinuclear core as magnetically isolated, the extended networks formed by hydrogen bonds take part in the intermolecular antiferromagnetic interaction and may cause deviation from this magneto-structural relationship. However, this correlation revealed that the increase of the interaction parameter J can be related to a decrease in  $\alpha$  and tends to vanish ( $J = 0.8 \text{ cm}^{-1}$ ) when  $\alpha$  approaches a value of 47.4° [77]. Based on the literature [76], it appears that the highest exchange parameters ( $I = 10.1 \text{ cm}^{-1}$ ) are associated with the lowest value  $\alpha$  (1.78°) The comparisons of the structural and magnetic characteristics in the CuO<sub>2</sub>Gd bridging network reported in the literature are listed in Table 4. Increasing the distortion from planarity of similar bridging system causes a decrease of I values.

The magnetic susceptibility  $\chi_m T$  of Cu<sup>II</sup>Tb<sup>III</sup> (**2**) has been also measured in the temperature range of 1.8–300 K in a 0.5 *T* of applied magnetic field. The data obtained for complex **2** are represented in Figs. 8 and 9. The values Curie and Weiss constants determined from the relation  $1/\chi_m = f(T)$  over temperature range 1.8–300 K are equal to 12.71 cm<sup>3</sup> mol<sup>-1</sup> and 1.96 K, respectively. At the room temperature, the  $\chi_m T$  product is equal to 12.61 cm<sup>3</sup> mol<sup>-1</sup> K, which is slightly larger than the value



Fig. 9. Field dependence of the magnetization for complex 2. The dashed line is the Brillouin function for two independent S = 1/2 and S = 4 systems.

(12.22 cm<sup>3</sup> mol<sup>-1</sup> K) expected for a pair of noninteracting Cu<sup>II</sup>  $(S = 1/_2)$  and Tb<sup>III</sup>  $(4f^8, f = 6, S = 3, L = 3, {}^7F_6)$  ions. As the temperature is lowered,  $\chi_m T$  gradually increases to reach a value of 14.61 cm<sup>3</sup> mol<sup>-1</sup> K at 10 K. The profile of the  $\chi_m T$  versus T curve is strongly suggestive of the occurrence a ferromagnetic Cu<sup>II</sup>-Tb<sup>III</sup> interaction in 10–300 K temperature range. Below 10 K, the  $\chi_m T$ values are decreased to 9.37 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K which may be attributed to zero-field splitting (ZFS) effects of the S = 9/2 ground state and/or intermolecular interactions. A quantitative analysis of complex 2 is not possible, due to the orbital momentum of the terbium(III) ion [80,81]. Similar to the trend found for the dinuclear Cu<sup>II</sup>Gd<sup>III</sup> complex, **2** exhibits an apparent ferromagnetic interaction for the similar dihedral angles ( $\alpha = 2.62^{\circ}$ ). For **2** the field dependence of the magnetization M at 2 K is shown in Fig. 9. The increase of the field up to 5 T results in a magnetization value above 6  $\mu_{\rm B}$ The M = f(H) is situated below the Brillouin function constructed for two independent S = 1/2 and S = 4 systems. This fact evidences an antiferromagnetic interaction and/or presence of zero - field splitting effect for Tb<sup>III</sup> ions.

#### 4. Conclusion

The heteronuclear Cu<sup>II</sup>Gd<sup>III</sup> (1) and Cu<sup>II</sup>Tb<sup>III</sup> (2) compounds are isostructural. In both complexes, the lanthanide(III) center has an O<sub>9</sub> coordination environment forming a slightly distorted tricapped trigonal prism. The discrete dinuclear units interact through O-H...O hydrogen bonds forming layers between which short Br...O contacts are observed. The dinuclear Cu<sup>II</sup>Gd<sup>III</sup> (1) and Cu<sup>II</sup>Tb<sup>III</sup> (2) compounds exhibit ferromagnetic interactions. Consideration of the magnetic and structural data obtained for various dinuclear Cu-Gd complexes leads to a correlation between the magnitude of the magnetic interaction (coupling constant *I* value) and the exponential of the dihedral angle  $\alpha$  between the two O-Cu-O and O-Gd-O fragments of the bridging CuO<sub>2</sub>Gd network. The occurrence of a ferromagnetic interaction between Cu<sup>II</sup> and Gd<sup>III</sup>/Tb<sup>III</sup> ions of the dinuclear entity is supported by the field dependence of the magnetization at 2 K.

## **Appendix A. Supplementary material**

CCDC 820671, 820669 and 820670 contains the supplementary crystallographic data for compounds 0, 1 and 2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.017.

#### References

- [1] A. Jana, S. Majumder, L. Carrella, M. Nayak, T. Weyhermueller, S. Dutta, D. Schollmeyer, E. Rentschler, R. Koner, S. Mohanta, Inorg. Chem. 49 (2010) 9012. A.M. Atria, Y. Moreno, E. Spodine, M.T. Garland, R. Baggio, Inorg. Chim. Acta 335 (2002) 1.
- [3] R. Koner, G.H. Lee, Y. Wang, H.H. Wei, S. Mohanta, Eur. J. Inorg. Chem. (2005) 1500.
- [4] C. Benelli, D. Gatteschi, Chem. Rev. 102 (2002) 2369.
- W. Shi, X.Y. Chen, B. Zhao, A. Yu, H.B. Song, P. Cheng, H.G. Wang, D.Z. Liao, S.P. [5] Yan, Inorg. Chem. 45 (2006) 3949.
- [6] J.H. Wang, P.F. Yan, G.M. Li, J.W. Zhang, P. Chen, M. Suda, Y. Einaga, Inorg. Chim. Acta 363 (2010) 3706.
- Y.T. Li, C.W. Yan, X.C. Zeng, Trans. Met. Chem. 26 (2001) 110.
- [8] M. Schley, S. Fritzsche, P. Lonnecke, E. Hey-Hawkins, Dalton Trans. 39 (2010) 4090.
- G. Novitchi, S. Shova, A. Caneschi, J.P. Costes, M. Gdaniec, N. Stanica, Dalton [9] Trans. (2004) 1194.
- [10] T. Gao, P.F. Yan, G.M. Li, G.F. Hou, J.S. Gao, Chim. Acta 361 (2008) 2051.
- [11] X.P. Yang, R.A. Jones, W.K. Wong, V. Lynch, M.M. Oye, A.L. Holmes, Chem. Commun. (2006) 1836.
- [12] J. Paulovic, F. Cimpoesu, M. Ferbinteanu, K. Hiro, J. Am. Chem. Soc. 126 (2004) 3321.
- [13] X. Yang, R.A. Jones, Q. Wu, M.M. Oye, W.K. Lo, W.K. Wong, A.L. Holmes, Polyhedron 25 (2006) 271.
- [14] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, New J. Chem. (1998) 1525.
- [15] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, Inorg. Chem. 35 (1996) 2400.
- [16] C.T. Zeyrek, A. Elmali, Y. Elerman, J. Mol. Struct. 740 (2005) 47.
- [17] O. Margeat, P.G. Lacroix, J.P. Costes, B. Donnadieu, C. Lepetit, Inorg. Chem. 43 (2004) 4743
- [18] J.P. Costes, B. Donnadieu, R. Gheorghe, G. Novitchi, J.P. Tuchagues, L. Vendier, Eur. J. Inorg. Chem. (2008) 5235.
- [19] S. Akine, T. Matsumoto, T. Taniguchi, T. Nabeshima, Inorg. Chem. 44 (2005) 3270
- [20] M. Sakamoto, Y. Nishida, A. Matsumoto, Y. Sadaoka, M. Sakai, Y. Fukuda, M. Ohba, H. Sakiyama, N. Matsumoto, H. Okawa, J. Coord. Chem. 38 (1996) 347.
- S. Mohanta, H.H. Lin, C.J. Lee, H.H. Wei, Inorg. Chem. Commun. 5 (2002) 585. [21]
- [22] A. Elmali, Y. Elerman, J. Mol. Struct. 737 (2005) 29.
- [23] J.P. Costes, F. Dahan, C. R. Acad. Sci. Paris, Chimie/Chemistry 4 (2001) 97.
- [24] J.P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 165.
- [25] H. Wang, D. Zhang, Z.H. Ni, X. Li, L. Ti, J. Jiang, Inorg. Chem. 48 (2009) 5946.
- [26] H. Kara, Y. Elerman, P. Prout, Z. Naturforsch, Z. Naturforsch B 55 (2000) 1131. [27] J.P. Costes, G. Novitchi, S. Shova, F. Dahan, J.P. Bruno Donnadieu, J.P. Tuchagues,
- Inorg. Chem. 43 (2004) 7792.
- [28] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, Inorg. Chem. 36 (1997) 3429. [29] J.P. Costes, F. Dahan, B. Donnadieu, J. Garcia-Tojal, J.P. Laurent, Eur. J. Inorg. Chem. (2001) 363.
- [30] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, Inorg. Chem. 36 (1997) 930.
- [31] M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Nishida, Y. Sakiyama, M. Sakai, Y. Sadaoka, M. Ohba, H. Okawa, J. Chem. Soc., Dalton Trans. (2000) 259.
- [32] R.E.P. Winpenny, Chem. Soc. Rev. (1998) 447.
- A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D.J. Gatteschi, J. Am. Chem. [33] Soc. 107 (1985) 8128.
- [34] C. Benelli, M. Murrie, S. Parson, R.E.P. Winpenny, J. Chem. Soc., Dalton Trans. (1999) 4125.
- [35] R. Koner, H.H. Lin, H.H. Wei, S. Mohanta, Inorg. Chem. 44 (2005) 3524. [36] S. Kyatskaya, J.R.G. Mascaros, L. Bogani, F. Hennrich, M. Kappes, W.
- Wernsdorfer, M. Ruben, J. Am. Chem. Soc. 131 (2009) 15143. [37] A. Figuerola, C. Diaz, J. Ribas, V. Tangoulis, J. Granell, F. Lloret, J. Mahia, M.
- Maestro, Inorg. Chem. 42 (2003) 5274.
- [38] J.P. Costes, L. Vendier, Eur. J. Inorg. Chem. (2010) 2768.
- [39] M. Ryazanov, V. Nikiforov, F. Lloret, M. Julve, N. Kuzmina, A. Gleizes, Inorg. Chem. 41 (2002) 1816.
- F.Z.C. Fellah, J.P. Costes, F. Dahan, C. Duhayon, G. Novitchi, J.P. Tuchagues, L. [40] Vendier, Inorg. Chem. 47 (2008) 6444.
- [41] G. Novitchi, J.P. Costes, B. Donnadieu, Eur. J. Inorg. Chem. (2004) 1808.
- [42] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, Inorg. Chem. 39 (2000) 169.
- [43] J.P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 5994.
- [44] R. Watanabe, K. Fujiwara, A. Okazawa, G. Tanaka, S. Yoshii, H. Nojiri, T. Ishida, Chem. Commun. 47 (2011) 2110.
- [45] T. Kajiwara, M. Nakano, S. Takaishi, Masahiro Yamashita, Inorg. Chem. 47 (2008) 8604.
- [46] A. Okazawa, R. Watanabe, M. Nezu, T. Shimada, S. Yoshii, H. Nojiri, T. Ishida,
  - Chem. Lett. 39 (2010) 1331. [47] J.P. Costes, J.M. Clemente-Juan, F. Dahan, J. Milon, Inorg. Chem. 43 (2004) 8200.
  - [48] J.P. Costes, F. Dahan, W. Wernsdorfer, Inorg. Chem. 45 (2006) 5.

  - [49] J.P. Costes, S. Shova, W. Wernsdorfer, Dalton Trans. (2008) 1843.
  - S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba, J. Mrozinski, J. Am. Chem. Soc. [50] 126 (2004) 420.
  - [51] O. Kahn, Molecular Magnetism, Willey-VCH, 1993.

- [52] Oxford Diffraction, Xcalibur CCD System, CRYSALIS Software System, Version 1.171, Oxford Diffraction Ltd., 2009.
- [53] R.C. Clark, J.S. Reid, Acta Crystallogr., Sect. A51 (1995) 887.
- [54] G.M. Sheldrick, Acta Crystallogr., Sect. A64 (2008) 112.
- [55] L.J. Faruggia, J. Appl. Crystallogr. 32 (1999) 837.
- [56] ORTEP3 for Windows: L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [57] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van De Streek, J. Appl. Crystallogr. 39 (2006) 453.
- [58] Diamond Crystal and Molecular Structure Visualization Crystal Impact, K. Brandenburg, H. Putz GbR, Rathausgasse 30, D-53111 Bonn.
- [59] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, Toronto, 1997.
- [60] O. Pouralimardan, A. Chamayou, C. Janiak, H. Hosseini-Monfared, Inorg. Chim. Acta 360 (2007) 1599.
- [61] G.B. Roy, Inorg. Chim. Acta 362 (2009) 1709.
- [62] M. Imran, L. Mitu, S. Latif, Z. Mahmood, I. Naimat, S.S. Zaman, S. Fatima, J. Serb. Chem. Soc. 75 (2010) 1075.
- [63] G.G. Mohamed, C.M. Sharaby, Spetrochim. Acta A 66 (2007) 949.
- [64] K.N. Kumar, R. Ramesh, Spetrochim. Acta A 60 (2004) 2913.
- [65] A. Dziewulska-Kułaczkowska, J. Therm. Anal. Calorim. 101 (2010) 1019.
- [66] J.S. Rutherford, Acta Chim. Hung. 134 (1997) 395.

- [67] L. Fabian, A. Kalman, Acta Crystallogr., Sect. B55 (1999) 1099.
- [68] F.H. Allen, Acta Crystallogr., Sect. B58 (2002) 380.
   [69] J.P. Costes, F. Dahan, G. Novitchi, V. Arion, S. Shova, J. Lipkowski, Eur. J. Inorg.
- Chem. (2004) 1530.
- [70] J.P.M. Lommerse, A.J. Stone, R. Taylor, F.H. Allen, J. Am. Chem. Soc. 118 (1996) 3108.
- [71] B.E. Myers, L. Berger, S.A. Friedberg, J. Appl. Phys. 40 (1969) 1149.
- [72] A. Bencini, EPR of Exchange Couples System, Springer-Verlag, Berlin, 1990.
- [73] F.Z. Chiboub Fellah, J.P. Costes, C. Duhayon, J.C. Daran, J.P. Tuchagues, Polyhedron 29 (2010) 2111.
- [74] O. Song Gao, H. Borgmeier, H. Lueken, Acta Phys. Pol. A 90 (1996) 393.
- [75] A. Elmali, Y. Elerman, Z. Naturforsch. 59b (2004) 535.
- [76] R.H. Bailes, M. Calvin, J. Am. Chem. Soc. 69 (1947) 1886.
- [77] M. Sasaki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nisahida, Y. Sadako, M. Ohba, H. Okawa, Chem. Lett. (1998) 911.
- [78] F. He, M.-L. Tong, X.-M. Chen, Inorg. Chem. 44 (2005) 8285.
- [79] C. Benelli, A.J. Blake, P.E.Y. Milne, J.M. Rawson, R.E.P. Winpenny, Chem. Eur. J. 1 (1995) 614.
- [80] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, Chem. Eur. J. 4 (1998) 1616.
- [81] M.L. Kahn, C. Mathonière, C.O. Kahn, Inorg. Chem. 38 (1999) 3692.