

# Reaction of a manganese(III)-Schiff base complex with gadolinium nitrate: synthesis, structure and magnetic properties of an ionic species $[\text{LMn}(\text{H}_2\text{O})_2][\text{Gd}(\text{NO}_3)_5(\text{MeOH})]$ ( $\text{H}_2\text{L} = 1,3\text{-bis}((3\text{-methoxysalicylidene})\text{amino})\text{-}2,2'\text{-dimethylpropane}$ )

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The crystal structure of an ionic entity formulated  $\{[\text{LMn}(\text{H}_2\text{O})_2][\text{Gd}(\text{NO}_3)_5(\text{MeOH})]\}$  resulting from the reaction of a manganese(III) Schiff-base complex ( $\text{H}_2\text{L} = 1,3\text{-bis}((3\text{-methoxysalicylidene})\text{amino})\text{-}2,2'\text{-dimethylpropane}$ ) with  $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  has been determined. The manganese(III) ion exhibits an octahedral geometry where the basal plane involves the  $\text{N}_2\text{O}_2$  inner donor set of the Schiff base and the apical positions are occupied by the water oxygen atoms. The gadolinium(III) ion is ten-coordinate to four bidentate nitrate groups, one monodentate nitrate group and one methanol oxygen atom. As expected from the structural data, the magnetic study confirms the absence of  $\text{Mn} \cdots \text{Mn}$  and  $\text{Mn} \cdots \text{Gd}$  interactions. Indeed the metal ions are separated by large distances without any material support between them. The  $\text{Mn}^{\text{III}}$  ZFS, which is the only active parameter, has to be taken into account to fit the experimental data at low temperature ( $D = -4.58 \text{ cm}^{-1}$ ). The negative sign is in agreement with the tetragonal elongation of the manganese environment.

## Introduction

The preparation of heteronuclear complexes containing both 4f and 3d ions has attracted special attention in view of their magnetic and electronic properties.<sup>1</sup> Indeed, the synthesis of discrete heterodinuclear complexes affords simple models to understand the respective influences of two different metal centres in modulating the electronic, magnetic and electrochemical properties of such compounds. Compartmental ligands, containing two phenoxo oxygen atoms which may act as endogenous bridging units and display specific stereochemical preferences for the two different metal ions have been particularly used.<sup>2</sup> The methoxy derivatives of salen ( $\text{H}_2\text{salen} = N,N'\text{-bis}(\text{salicylidene})\text{ethylenediamine}$ ) (Fig. 1) contain an inner site with N- and O-donor chelating centers suitable for the

complexation of d-block ions, and an outer coordination site with four O-donor atoms which is larger than the inner one and able to incorporate larger oxophilic ions, such as lanthanide ones.<sup>3</sup>

In the past few years, several heterodinuclear complexes of salen derivatives containing orbitally non-degenerate  $\text{Cu}^{\text{II}}/\text{Gd}^{\text{III}}$ ,<sup>4</sup>  $\text{V}^{\text{IV}}/\text{Gd}^{\text{III}}$ ,<sup>5</sup>  $\text{Ni}^{\text{II}}/\text{Gd}^{\text{III}}$ ,<sup>6</sup> and orbitally degenerate  $\text{Fe}^{\text{II}}/\text{Gd}^{\text{III}}$ ,<sup>7</sup> and  $\text{Co}^{\text{II}}/\text{Gd}^{\text{III}}$ <sup>8</sup> systems have been studied. We have now focused our research on the heterodinuclear Mn/Gd complexes as an extension of our previous works. The current literature contains few structural studies on manganese/gadolinium heteropolynuclear complexes<sup>9</sup> and no reports on the magnetic behaviour of heterodinuclear entities. Furthermore, it appears that the Mn/Gd/salen analog systems have been unexplored. Herein we report our work aiming at filling in this gap. Although we have not succeeded in isolating a dinuclear MnGd species, we have characterized an ionic entity containing Mn and Gd ions included in cationic and anionic components, respectively.

## Results and discussion

### $[\text{LMn}(\text{H}_2\text{O})_2][\text{Gd}(\text{NO}_3)_5(\text{MeOH})]$ 1

A view of the molecular structure is shown in Fig. 2 and the most relevant interatomic distances and angles are listed in Table 1. The asymmetric unit is comprised of two cationic  $[\text{LMn}(\text{H}_2\text{O})_2]^+$  and one dianionic  $[\text{Gd}(\text{NO}_3)_5(\text{CH}_3\text{OH})]^{2-}$  component, L being the fully deprotonated form of  $N,N'\text{-bis}((3\text{-methoxysalicylidene})\text{-}1,3\text{-diaminopropane})$ . Within each cationic species, the manganese(III) ion exhibits an elongated octahedral geometry. The two nitrogen and two phenoxo oxygen atoms of the ligand are coordinated in the equatorial plane while the axial positions are occupied by the oxygen atoms of two water molecules. The Mn–N and Mn–O bond lengths of the two cationic entities (Mn1 and Mn2) are very similar, the equatorial bonds being slightly shorter (0.01–0.02 Å) for Mn2. On the contrary, one axial Mn–O(water) is shorter by 0.02 Å for

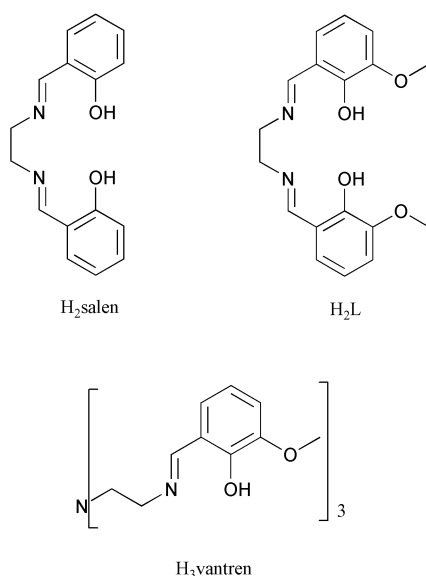
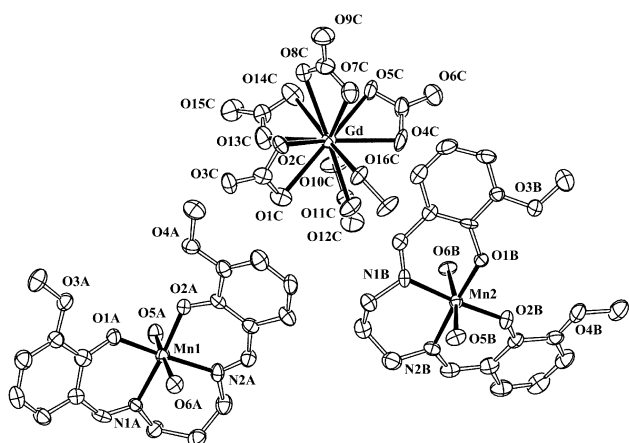


Fig. 1 Schematic representation of the ligands used in this work.

**Table 1** Selected bond lengths (Å) for [LMn(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Gd(NO<sub>3</sub>)<sub>5</sub>(MeOH)].

Mn(1)–O(1A)	1.898(2)	Mn(2)–O(1B)	1.876(2)
Mn(1)–O(2A)	1.913(2)	Mn(2)–O(2B)	1.902(2)
Mn(1)–N(1A)	2.047(2)	Mn(2)–N(1B)	2.036(2)
Mn(1)–N(2A)	2.042(2)	Mn(2)–N(2B)	2.026(2)
Mn(1)–O(5A)	2.191(2)	Mn(2)–O(5B)	2.213(2)
Mn(1)–O(6A)	2.218(2)	Mn(2)–O(6B)	2.219(2)
Gd–O(1C)	2.610(2)	Gd–O(2C)	2.466(2)
Gd–O(4C)	2.500(2)	Gd–O(5C)	2.546(2)
Gd–O(7C)	2.529(2)	Gd–O(8C)	2.528(2)
Gd–O(10C)	2.485(2)	Gd–O(11C)	2.543(2)
Gd–O(13C)	2.440(2)	Gd–O(16C)	2.430(2)
Gd ⋯ O(14C)	2.965(2)		

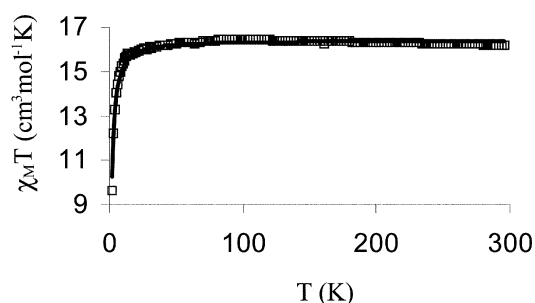
**Fig. 2** Molecular structure of [LMn(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Gd(NO<sub>3</sub>)<sub>5</sub>(MeOH)] **1** with thermal ellipsoids at 70% probability level.

Mn1. The gadolinium(III) ion is ten-coordinate, bonded to four nitrate groups acting as bidentate ligands ( $\eta^2$ -coordination), to one nitrate group acting as a monodentate donor and to a methanol oxygen atom. The shortest Gd–O bond involves the methanol oxygen atom (2.430(2) Å) while the Gd–O nitrate bond lengths range from 2.466(2) to 2.610(2) Å. For the monodentate nitrate anion, the Gd–O distance of 2.965(2) Å is not considered as a bond. The Mn ⋯ Gd distances within the asymmetric unit are large, 9.340(1) and 10.287(1) Å for Mn2 ⋯ Gd and Mn1 ⋯ Gd, respectively, and 10.400(1) Å for Mn1 ⋯ Mn2. Along the *a* axis, the cationic entities are stacked up in a head-to-tail fashion, as a consequence of a weak  $\pi$ – $\pi$  interaction between the aromatic rings of the ligands. The head-to-tail conformation, probably due to the presence of water molecules around the Mn centres, results in Mn ⋯ Mn

distances of 5.2132(4) and 5.2343(3) Å for Mn1 ⋯ Mn1 and Mn2 ⋯ Mn2, respectively. The ligand is not planar, and the cationic entities have a boat conformation, the aromatic rings being on the same (out)side of the N<sub>2</sub>O<sub>2</sub> coordination site. The six-membered diamine ring adopts a chair conformation. Although the chair conformation of a six-membered diamine ring is not chiral the interaction of such non-chiral rings with the metal centre generates chirality.<sup>10</sup> The combination of the boat conformation of the cationic [LMn(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> entities with the orientation of the C–C–C plane of the diamino rings yields two conformers. As only one conformer is present in the crystal structure, the C–C–C plane pointing toward the phenyl rings, our complex crystallizes in a chiral group, *P*2<sub>1</sub>2<sub>1</sub>. Hydrogen bonds between the water molecules axially linked to the Mn ions and the methoxy oxygen atoms of the neighbouring cationic entity stabilize this structure (Table 2).

### Magnetic properties

The magnetic susceptibility  $\chi_M$  of complex **1** has been measured in the 2–300 K temperature range in a 1.0 T applied magnetic field. The data obtained for complex **1** are shown in Fig. 3. At 300 K the  $\chi_M T$  product is equal to 14.35 cm<sup>3</sup> mol<sup>−1</sup> K, which is slightly larger than the expected 13.85 cm<sup>3</sup> mol<sup>−1</sup> K value for two non-interacting *S* = 2 (Mn) and one *S* = 7/2 (Gd) spins. As the temperature is lowered,  $\chi_M T$  is constant from room temperature to 40 K, it decreases smoothly down to 14 K (13.85) and then more steeply, reaching a value of 10.71 cm<sup>3</sup> mol<sup>−1</sup> K at 2 K. This behaviour is consistent with the absence of magnetic interaction between the different magnetic centres, the  $\chi_M T$  decrease at low temperature being attributable to zero field splitting (ZFS) effects originating from the Mn<sup>III</sup> ion. The Gd<sup>III</sup> ion, with a <sup>8</sup>S<sub>7/2</sub> ground state devoid of any orbital momentum, has no contribution to the ZFS. Owing to the structural data no Mn ⋯ Gd interaction is expected since the ions are separated

**Fig. 3** Thermal dependence of  $\chi_M T$  for complex **1**. The solid line represents the best fit of the experimental data (see text).**Table 2** Hydrogen bonds for [LMn(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Gd(NO<sub>3</sub>)<sub>5</sub>(MeOH)]

D	H	D–H/Å	A	H ⋯ A/Å	D ⋯ A/Å	D–H ⋯ A/°
O(5A)	H(51A)	0.95(2)	O(3A <sup>III</sup> )	1.83(3)	2.757(3)	165(3)
	H(52A)	0.97(3)	O(4A <sup>III</sup> )	1.85(2)	2.770(3)	158(2)
O(6A)	H(61A)	0.97(2)	O(2A <sup>II</sup> )	2.00(2)	2.847(3)	145(2)
	H(61A)	0.97(2)	O(4A <sup>II</sup> )	2.19(2)	2.969(3)	136(2)
	H(62A)	0.99(3)	O(1A <sup>II</sup> )	2.00(3)	2.884(2)	147(2)
	H(62A)	0.99(3)	O(3A <sup>II</sup> )	2.32(3)	3.077(3)	132(2)
O(5B)	H(51B)	0.95(2)	O(3B <sup>I</sup> )	1.98(3)	2.827(3)	147(3)
	H(52B)	0.96(2)	O(4B <sup>I</sup> )	1.83(2)	2.774(3)	165(3)
O(6B)	H(61B)	0.96(2)	O(2B <sup>IV</sup> )	1.96(3)	2.850(2)	154(2)
	H(61B)	0.96(2)	O(4B <sup>IV</sup> )	2.38(3)	3.041(3)	126(2)
	H(62B)	0.94(3)	O(3B <sup>IV</sup> )	1.97(2)	2.851(2)	155(3)
	H(62B)	0.94(3)	O(1B <sup>IV</sup> )	2.21(3)	2.864(2)	126(2)
O(16C)	H(16C)	0.89(3)	O(14C <sup>V</sup> )	2.09(3)	2.821(3)	138(3)

Symmetry operations: I 1/2 + *x*, 1/2 – *y*, 1 – *z*; II 1/2 + *x*, 3/2 – *y*, 1 – *z*; III –1/2 + *x*, 3/2 – *y*, 1 – *z*; IV –1/2 + *x*, 1/2 – *y*, 1 – *z*; V 1 + *x*, *y*, *z*.

by large distances of *ca.* 10 Å without any material support between them. On the contrary, Mn ··· Mn interactions *via* the hydrogen bond system along the anionic chains could operate. Nevertheless, a simple Hamiltonian ( $H = D_{\text{Mn}} S_z^2$ ) taking only into account axial single-ion ZFS without any Mn ··· Mn interaction yields a satisfying fit and allows the *D* term to be evaluated. The best fit for complex **1** yields a *D* value of  $-4.58 \text{ cm}^{-1}$  which is in agreement with the range of values found in the literature.<sup>11</sup> The negative sign is in agreement with the tetragonal elongation of the manganese environment.<sup>11</sup>

## Discussion

The most surprising result is the isolation of an ionic species instead of the usual heterodinuclear 3d–Gd complexes obtained with the same ligand coordinated to copper(II),<sup>4</sup> high-spin nickel(II),<sup>6</sup> cobalt(II) and cobalt(III),<sup>8</sup> iron(II)<sup>7</sup> and VO(II)<sup>5</sup> ions. Similar ligands with different diamino chains are also able to give other examples of heterodinuclear complexes with nickel low spin,<sup>3a</sup> iron(III)<sup>12</sup> and zinc(II).<sup>13</sup> At first sight, it is difficult to explain this behaviour. Until now, we have been unable to isolate and characterize any Mn(II)–Gd(III) species, even when carrying out the preparations in a glove-box and using the conditions that yielded the Fe(II)–Gd(III)<sup>7</sup> and Co(II)–Gd(III)<sup>8</sup> complexes. The resulting yellow complex appears to be correctly formulated as  $\text{H}_2\text{LGd}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ,<sup>13</sup> implying occurrence of an exchange reaction between the Mn<sup>II</sup> and Gd<sup>III</sup> ions. A closer look at these results indicates that the majority of our dinuclear M–Gd complexes involve 3d centres in the +2 oxidation state. Indeed, we have been less successful in the preparation of 3d–Gd complexes involving a 3d ion in the +3 oxidation state. The simplest way to explain this behaviour is the repulsive effect of the cationic  $[\text{LMn}(\text{H}_2\text{O})_2]^+$  species toward the gadolinium ion. Very recently, we have shown that oxo–Fe(III) complexes<sup>14</sup> are able to coordinate Gd ions and that Co(III)–Gd entities with two additional acetato bridges do exist.<sup>8</sup> If the oxo–Fe(III) complex can be considered as a neutral starting material, the preparation of Co–Gd dinuclear species in air should be considered as a positive factor for a successful synthesis of the equivalent Mn<sup>III</sup>–Gd complex. However, using similar preparation conditions, *i.e.* starting with manganese(II) ions yielded the species described in this report, and not the expected Mn<sup>III</sup>–Gd complex. The structural determination confirms that the ligand coordinated to the Mn centre is not planar and presents a boat conformation. Is this deformation sufficient to prevent coordination of the Gd ions? A closer look at the inner N<sub>2</sub>O<sub>2</sub> and outer O<sub>4</sub> coordination sites confirms that the distances between the imine nitrogen, deprotonated phenoxo and methoxy oxygen atoms are very close in the present case (3.000(1), 2.630(1), 4.734(1) Å and 3.000(1), 2.603(1), 4.707(1) Å for Mn1 and Mn2, respectively) as well as in the genuine Cu–Gd (2.961(1), 2.490(1), 4.852(1) Å),<sup>4b</sup> Ni–Gd (3.008(1), 2.575(1), 4.855(1) Å),<sup>6</sup> Fe–Gd (3.128(1), 2.576(1), 4.887(1) Å)<sup>7</sup> and Co–Gd complexes (3.061(1), 2.549(1), 4.893(1) Å)<sup>8</sup> obtained with the same Schiff-base ligand. This structural comparison does not allow to explain the synthetic failure as resulting from the ligand deformation. Keeping this in mind, we have tried to react gadolinium ions with a neutral complex, Mn(III)(vantren)<sup>15</sup> (the tripodall H<sub>3</sub>vantren ligand (Fig. 1) was prepared by reaction of *o*-vanillin and tris(2-aminoethyl)amine).<sup>16</sup> This reaction did not yield the expected (vantren)MnGd(NO<sub>3</sub>)<sub>3</sub> complex but a dinuclear (vantren)GdGd(NO<sub>3</sub>)<sub>3</sub> species, as confirmed by magnetic measurements and FAB mass spectrometry.<sup>17</sup> This result is again in contrast with Fe<sup>III</sup> chemistry where isolation of the (vantren)Fe<sup>III</sup>–Gd(NO<sub>3</sub>)<sub>3</sub> complex is achieved.<sup>12</sup>

In conclusion, we have prepared and studied an original ionic complex while attempting unsuccessfully to use Schiff-base ligands to isolate heterodinuclear Mn–Gd complexes. Neither the size of the outer O<sub>4</sub> coordination site, nor the ionic radius of

Mn<sup>III</sup>, seem to be responsible for this failure. If repulsion between  $[\text{LMn}(\text{H}_2\text{O})_2]^+$  cationic species and Gd<sup>3+</sup> can not be avoided, it is quite clear that the chemistry of Mn<sup>III</sup> ions with such Schiff bases greatly differs from the Fe<sup>III</sup> and Co<sup>III</sup> chemistry. Surprisingly, an exchange reaction between Mn<sup>II</sup> and Gd<sup>III</sup> ions takes place with salen type Schiff bases while it also occurs between Mn<sup>III</sup> and Gd<sup>III</sup> ions with tripodall ligands. The magnetic behaviour of the ionic entity agrees with the structural determination. A Mn–Gd interaction is precluded by the ionic nature and the insulation of both metal ions positioned at large distances. An Mn–Mn interaction is also precluded by the large Mn ··· Mn distance, and the absence of interaction through the hydrogen bonds.

## Experimental

### Preparation of the complexes

Starting materials were purchased from Acros Organics (*o*-vanillin) and Aldrich (1,3-diamino-2,2'-dimethylpropane, manganese(II) acetate tetrahydrate and gadolinium nitrate hexahydrate), and used without further purification. The ligand was prepared as described in the literature.<sup>18</sup> The complex was synthesized in the open atmosphere.

### $\{[\text{LMn}(\text{H}_2\text{O})_2]_2[\text{Gd}(\text{NO}_3)_5(\text{MeOH})]\}$ **1**

Manganese(II) acetate (1 mmol, 0.25 g) was added as a solid to a solution of the Schiff base in methanol (1 mmol, 0.37 g). The brown solution was stirred for 15 min and then, an equimolar amount of gadolinium nitrate (1 mmol, 0.45 g) was added with stirring, yielding a colour change. Green crystals suitable for X-ray studies were obtained by slow evaporation of the solvent. Anal. Found: C, 34.0; H, 3.9; N, 9.4. Calc. for  $\text{C}_{39}\text{H}_{52}\text{GdMn}_2\text{N}_{10}\text{O}_{31}$ : C, 34.4; H, 3.9; N, 9.3%. Selected IR bands ( $\text{cm}^{-1}$ ): 3392m, 1610s, 1555m, 1452s, 1384s, 1306s, 1256s, 1227s, 1072m, 857m, 733s.

### Physical measurements

Elemental analyses were carried out at the Laboratoire de Chimie de Coordination, France, for C, H and N. IR spectra were recorded on a GX system 2000 Perkin-Elmer spectrophotometer. Samples were run as KBr pellets.

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. All samples were 3 mm diameter pellets molded from ground crystalline samples. Magnetic susceptibility measurements were performed in the 2–300 K temperature range in a 1.0 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.<sup>19</sup> The magnetic susceptibility has been computed by exact calculation of the energy levels associated to the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry,<sup>20</sup> and with the MAGPACK program package<sup>21</sup> for magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.<sup>22</sup>

### Crystallography

Crystal data for  $\{[\text{LMn}(\text{H}_2\text{O})_2]_2[\text{Gd}(\text{NO}_3)_5(\text{MeOH})]\}$  **1**:  $\text{C}_{39}\text{H}_{52}\text{GdMn}_2\text{N}_{10}\text{O}_{28}$ ,  $M = 1362.03$ , orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a = 7.6348(4)$ ,  $b = 25.2598(13)$ ,  $c = 26.1515(12)$  Å,  $V = 5043.4(4)$  Å<sup>3</sup>,  $T = 180$  K,  $Z = 4$ ,  $D_c = 1.794$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.896$  mm<sup>-1</sup>, 45836 reflections collected, 14190 unique ( $R_{\text{int}} = 0.0418$ ). The final *R* values were  $wR(F^2) = 0.0546$  (all data) and  $R = 0.0306$  [ $F^2 > 2\sigma(F^2)$ ].

The selected crystal (green plate, 0.40 × 0.20 × 0.15 mm) was mounted on an Oxford-Diffraction Xcalibur diffractometer using a graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and equipped with an Oxford Instruments Cryojet cooler device. Data were collected<sup>23</sup> at 180 K with 4 runs ( $\phi = 0$ ,

90, 180, 270°) and  $\omega$  scans up to  $\theta = 30.39^\circ$  (153 frames for each run during a maximum time of 40 s). Gaussian absorption corrections<sup>24</sup> were applied ( $T_{\min, \max} = 0.5276, 0.7741$ ). The structures were solved by direct methods using SHELXS-97<sup>25</sup> and refined on  $F^2$  by full-matrix least-squares using SHELXL-97<sup>26</sup> with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model, except those bonded to the water and methanol oxygen atoms that were allowed to vary. Isotropic  $U_H$  were 1.1 times higher than those of the atom to which they are bonded. Scattering factors were taken from ref. 27. The molecular plots were obtained using the ZORTEP program.<sup>28</sup>

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See <http://www.rsc.org/suppdata/dt/b3/b303882c/> for crystallographic data in CIF or other electronic format

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