# Synthesis and structural and magnetic characterization of discrete phenolato and imidazolate bridged Gd(III)–M(II) [M = Cu, Ni] dinuclear complexes

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## Abstract

Three dinuclear complexes formed by the reaction of $Gd(hfa)_3$ (hfa is hexafluoroacetylacetonate) with Schiff base complexes of Cu(II) and Ni(II) have been synthesized and characterized. The crystal structures of the complexes [$Gd(hfa)_3M(prpen)$] {M = Cu(II (**1**)), Ni(II) (**2**)} are reported. ($H_2prpen$ is the Schiff base derived from the condensation of 2 equiv. of 2-hydroxypropiophenone and 1 equiv. of ethylenediamine.) Both **1** and **2** are discrete dinuclear complexes consisting of an eight coordinate Gd atom which is bridged to four coordinate M(II) via both phenolate oxygen atoms of the prpen ligand. The crystal structure shows there is no tendency toward dimerization between adjacent Cu(II) Schiff base units in **1**. Cryomagnetic measurements show a ferromagnetic interaction between Gd(III) and Cu(II) in **1** as predicted by theory with $J = 1.91$ cm$^{-1}$. The reaction of $Gd(hfa)_3$ with Ni(L) ($H_2L$ is the Schiff base derived from the condensation of 1 equiv. each of 5-chlorobenzophenone, 1,2-diaminobenzene, and 5-methyl-4-imidazolecarboxaldehyde) produced $Gd(hfa)_3Ni(L)$ (**3**) in which imidazolate is available to bridge Gd(III) and Ni(II). © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Gadolinium complexes; Dinuclear complexes; Ferromagnetism; Gadolinium imidazolate

## 1. Introduction

Since the mid 1980s, there have been several efforts to synthesize discrete heterodinuclear complexes of f and d block metals because of interest in their magnetic properties. The simplest f block metal to consider is Gd(III) since the $^8S_{7/2}$ free ion ground state of Gd(III) has no first order orbital momentum to complicate the magnetic analysis. There has therefore been a great deal of interest in the Gd(III)–M(d block) couple, especially Gd(III)–Cu(II). It has been predicted by Gatteschi [1], and observed in most cases reported so far, that the isolated Gd(III)–Cu(II) interaction will be ferromagnetic regardless of structural considerations. Most of the dinuclear complexes for which both structural and magnetic analyses have been reported thus far contain Gd(III) coupled to Cu(II) via phenolato, acetato, or acetonato donors. The Gd(III)–Cu(II) interactions in these cases have been found to be ferromagnetic as predicted. More recently, however, Costes et al. have reported the synthesis of an antiferromagnetically coupled Gd(III)–Cu(II) dinuclear complex in which Gd and Cu are unsymmetrically bridged by a phenolate oxygen atom and an oximato (N–O) group [2]. This result calls into question the assumption of ferromagnetism for every Gd(III)–Cu(II) couple and emphasizes the need for the synthesis and characterization of other Gd(III)–Cu(II) coupled systems.

The dinuclear complexes prepared in this work were all derived from the acid–base reaction of $Gd(hfa)_3 \cdot 2H_2O$ with a transition metal Schiff base as part of a general synthetic scheme designed to produce

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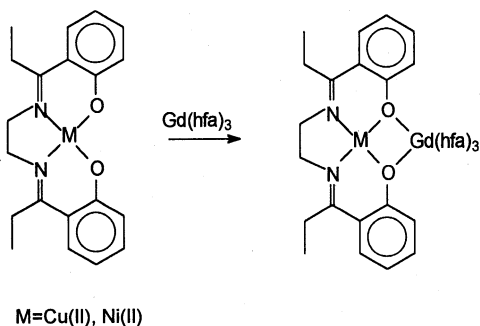
Scheme 1.

Gd–M dinuclears with phenolato, oxamato, or imidazolate bridging ligands. In this article we report the synthesis and structural and magnetic characterization of two Gd(III)–M(II) (M = Cu, Ni) dinuclear complexes in which the Gd and M(II) atoms are linked by phenolate oxygen atoms. We also report the synthesis of a novel imidazolate bridged Gd(III)–Ni(II) dinuclear complex.

The synthetic strategy followed for the phenolato bridged systems reacted a four coordinate M(II) Schiff base complex Mprpen (H$_2$prpen is the ligand derived from the condensation of 1 equiv. of ethylene diamine with 2 equiv. of 2-hydroxypropiophenone) with Gd(hfa)$_3$·2H$_2$O (hfa is hexafluoroacetylacetonate or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione). Binding of the acidic Gd(hfa)$_3$ moiety to the two phenolato oxygen atoms of the M(II) complex resulted in the dinuclear complexes (1) [Gd(hfa)$_3$Cu(prpen)] and (2) [Gd(hfa)$_3$Ni(prpen)] (Scheme 1). A symmetrical double phenolato bridged dinuclear complex of Gd(III) and Cu(II) similar to 1 has been prepared by Ramade et al. [3] by reaction of a similar Cu(II) Schiff base complex, Cusalen, (H$_2$salen is the ligand derived from the condensation of 1 equiv. of ethylene diamine with 2 equiv. of salicyladehyde) with Gd(hfa)$_3$·2H$_2$O. However, in this complex the copper atoms of adjacent dinuclear units are separated by relatively short distances, so that the Gd(III)–Cu(II) pairs are not perfectly isolated, but rather associated in dimeric units. This complicated the interpretation of the observed

magnetism because of the antiferromagnetic interaction between adjacent Cu centers. Addition of methylimidazole to the copper coordination sphere of the Gd(III)–Cu(II) pair broke up the dimeric interaction and produced a discrete dinuclear unit which exhibited the expected, although weak, ferromagnetic interaction between Gd(III) and *five* coordinate Cu(II). H$_2$prpen is identical to H$_2$salen except for the replacement of two H atoms in H$_2$salen with two ethyl groups in H$_2$prpen. This structural difference is sufficient to prevent a similar dimerization of Cuprpen molecules in 1 resulting in a discrete dinuclear complex.

The affinity of Gd(III) for oxygen donors has been utilized for the syntheses of the Gd(III)–Cu(II) complexes described above as well as most of the Gd(III)–Cu(II) dinuclears reported in the literature. There has been one report, however, of a dinuclear complex of Gd(III) and Cu(II) which employs imidazolate as a connecting ligand and which shows weak ferromagnetic coupling [4]. The Cu(II) imidazolate complex reported in this study is structurally similar to another M(II) complex which we have used successfully to form imidazolate bridged dinuclears of transition metals and therefore seemed a logical reagent to try in an attempt to prepare an imidazolate bridged Gd(III)–M(II) dinuclear. The acid/base reaction of Gd(hfa)$_3$·2H$_2$O with the nickel(II) complex of the Schiff base H$_2$L gave the dinuclear product (3) [Gd(hfa)$_3$Ni(L)] in which imidazolate is available for bridging the Gd(III) and Ni(II) metals (Scheme 2.). The analogous reaction of Cu(L) with Gd(hfa)$_3$ produced a product which did not give satisfactory analysis data.

In addition to the syntheses of 1, 2, and 3, the reactions of several transition metal hexafluoroacetylacetonates with Gd(salen)NO$_3$ were attempted. For the reactions of M(hfa)$_2$, where M = Co(II), Ni(II), or Cu(II), ligand exchange was observed. Products isolated from these reaction mixtures were identified as M(II)(salen). This result is consistent with the preference of Gd(III) for O donors and of Cu(II), Ni(II), and Co(II) for the N$_2$O$_2$ donor set of the salen ligand.
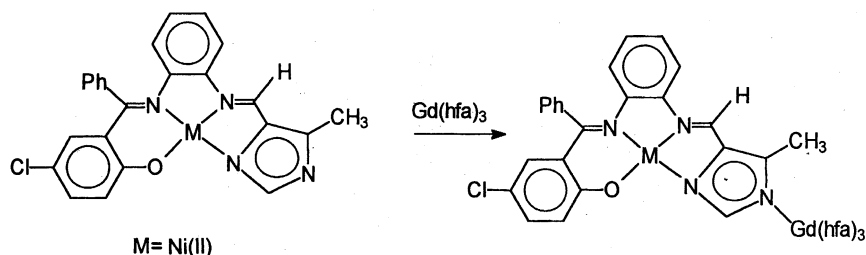


Scheme 2.

## 2. Experimental

### 2.1. General

Organic reagents, metal salts and solvents were obtained from Aldrich and used as received. The complexes, Cuprpen and Niprpen, were prepared as reported previously [5]. GdsalenNO$_3$ was prepared by the method reported by Costes et al. [6]. Gd(hfa)$_3$·H$_2$O was made as reported by Richardson [7]. Transition metal hexafluoroacetylacetonates, M(hfa)$_2$·2H$_2$O {M = Co(II), Ni(II) and Cu(II)}, were prepared by established procedures [8]. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. Elemental analyses were done by MHW laboratories.

### 2.2. Preparation of Gd(hfa)$_3$Cuprpen (1)

Cuprpen (0.0316 g, 0.0819 mmol) was dissolved in 10–15 ml of hot chloroform. Gd(hfa)$_3$·2H$_2$O (0.0655 g, 0.0805 mmol) in 10 ml CHCl$_3$ was added. The red solution was set aside. On standing overnight, well-formed, red crystals of 1 suitable for X-ray analysis had precipitated (0.0658 g, 0.0565 mmol, 70%). The presence of the hfa group was confirmed in the IR spectrum by strong absorption bands at 1148, 1207, and 1261 cm$^{-1}$ attributable to $\nu$CF$_3$. (Found: C, 36.23: H, 2.22: N, 2.21. C$_{35}$H$_{25}$CuF$_{18}$GdN$_2$O$_8$ requires C, 36.10: H, 2.16: N, 2.41%.)

### 2.3. Preparation of Gd(hfa)$_3$Niprpen (2)

Niprpen (0.0496 g, 0.130 mmol) and Gd(hfa)$_3$·2H$_2$O (0.1027 g, 0.126 mmol) were reacted as described above for the synthesis of 1. Afer standing overnight, the reaction mixture yielded large orange crystals of 2 suitable for X ray analysis (0.0713 g, 0.0615 mmol, 49%). The presence of the hfa group was confirmed in the IR spectrum by strong absorption bands at 1146, 1209, and 1259 cm$^{-1}$ attributable to $\nu$CF$_3$. (Found: C, 36.14: H, 1.86: N, 2.26. C$_{35}$H$_{25}$NiF$_{18}$GdN$_2$O$_8$ requires C, 36.26: H, 2.17: N, 2.42%.)
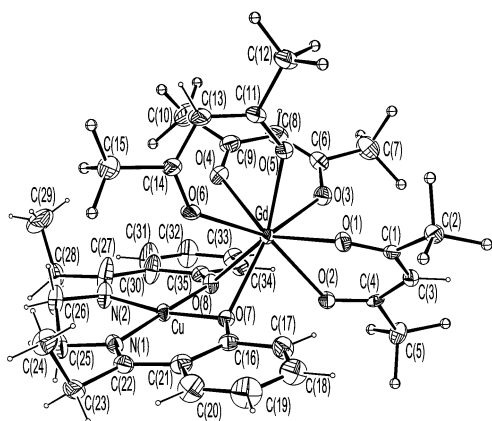
### 2.4. Preparation of Ni(L)

Ni(L) was prepared as described previously for M(CBP-PHEN-Im) [9] with the substitution of 4-methyl-5-imidazolecarboxaldehyde for 4(5)-imidazolecarboxaldehyde. An orange crystalline powder was obtained from ethanol. (85%. Found: C, 61.34: H, 4.11: N, 11.70. C$_{24}$H$_{17}$N$_4$ClONi requires C, 61.13: H, 3.63: N, 11.88%.)

### 2.5. Preparation of Gd(hfa)$_3$Ni(L) (3)

A suspension of Ni(L) (0.0823 g, 0.174 mmol) in about 120 ml methanol was heated and stirred. Not all of the solid dissolved. Gd(hfa)$_3$·2H$_2$O (0.1423 g, 0.175 mmol) in 5–10 ml of methanol was added. The remaining Ni(L) solid dissolved immediately. The reaction mixture was filtered while hot into a large beaker which was set aside to allow evaporation. After several days an orange solid (3) was removed by filtration (0.0707 g, 0.0566 mmol, 33%). The presence of the hfa group was confirmed in the IR spectrum by strong absorption bands at 1146, 1203, and 1256 cm$^{-1}$ attributable to $\nu$CF$_3$. (Found: C, 37.22: H, 1.85: N, 4.70. C$_{39}$H$_{20}$N$_4$ClGdF$_{18}$O$_7$Ni requires C, 37.48: H, 1.61: N, 4.48%.)

### 2.6. Structure determinations

Single-crystal experiments for 1 and 2 were carried out on an Enraf–Nonius FAST area detector diffractometer at 130 K by methods and procedures for small molecules standard in this lab [10]. A summary of determined parameters is given in Table 1. All reflections were reduced using Lorentz-polarization factors. The structures were solved by direct methods and refined against $F^2$ by the SHELXL-97 program [11]. Refinement of the two structures was routine except that for compound 1 one ethyl group (C(28) and C(29)) and a trifluoromethyl group were disordered.

Table 1
Crystallographic data

|  | 1 | 2 |
|---|---|---|
| Formula | C$_{35}$H$_{25}$CuF$_{18}$GdN$_2$O$_8$ | C$_{35}$H$_{25}$F$_{18}$GdN$_2$NiO$_8$ |
| Formula weight (amu) | 1164.36 | 1159.53 |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 12.9790(12) | 11.9888(12) |
| $b$ (Å) | 18.7319(15) | 12.8747(12) |
| $c$ (Å) | 17.1547(7) | 13.9288(10) |
| $\alpha$ (°) |  | 75.722(8) |
| $\beta$ (°) | 99.572(7) | 84.292(6) |
| $\gamma$ (°) |  | 80.524(5) |
| Volume (Å$^3$) | 4112.6(5) | 2051.2(3) |
| $Z$ | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 2.249 | 2.195 |
| Temperature (K) | 130(2) | 130(2) |
| Final $R$ indices ($I > 2\sigma(I)$) |  |  |
| $R_1$ | 0.0497 | 0.0432 |
| $wR_2$ | 0.1254 | 0.1044 |
| $R$ indices (all data) |  |  |
| $R_1$ | 0.0572 | 0.0501 |
| $wR_2$ | 0.1303 | 0.1086 |
| Goodnes-of-fit on $F^2$ | 1.083 | 1.043 |

Fig. 1. ORTEP diagram of complex **1**.

## 2.7. Magnetic measurements

Magnetic susceptibility data were collected on powdered samples of **1** and **2** using a Quantum Design SQUID magnetometer. Data were corrected for diamagnetism of the ligands estimated from Pascal's constants. A discussion of general magnetic susceptibility measurements and calibration techniques used can be found elsewhere [12]. Data were collected at a magnetic field of 500 Oe between 300 and 10 K.

## 3. Results and discussion
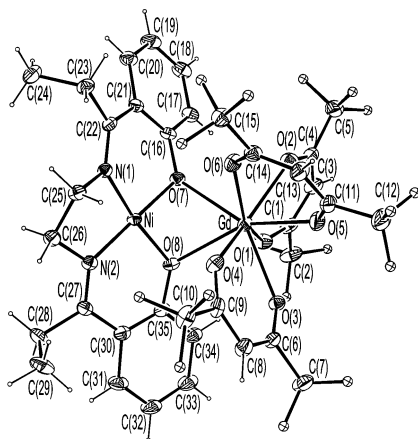
### 3.1. Crystal structures of **1** and **2**

Fig. 1 is an ORTEP diagram of **1**. For greater clarity the fluorine atoms are not labelled. Selected distances and bond angles for **1** and **2** are listed in Table 2. The Gd(III)–Cu(II) dinuclear unit is doubly bridged by the O atoms of the prpen ligand. The Gd–Cu distance is 3.2525(5) Å. The bridging network Gd O(7) O(8) Cu has a butterfly shape with a dihedral angle between the O(7) Gd O(8) and O(7) Cu O(8) planes of 137.8°. The coordination geometry about gadolinium is a distorted square antiprism of eight oxygen atoms, six from the three hfa ligands and two from the prpen ligand. The upper square consists of O(1) O(5) O(6) O(7) with an average Gd–O distance of 2.393 Å. The lower square consists of O(2) O(3) O(4) O(8) with an average Gd–O distance of 2.377 Å. The Cu atom and the two O and two N atoms of the prpen Schiff base ligand form a plane with deviations from the mean plane of $-0.05$ Å for Cu, 0.08 Å for O(7), $-0.06$ Å for O(8), $-0.05$ Å for N(1) and 0.08 Å for N(2).

Fig. 2 is an ORTEP diagram of the analogous complex, **2**. The Gd(III)–Ni(II) dinuclear unit is also doubly bridged by the O atoms of the prpen ligand with a dihedral angle between the O(7) Gd O(8) and O(7) Cu O(8) planes of 123.64°. The Gd–Ni distance is

3.0964(5) Å. Gadolinium is eight coordinate with a distorted square antiprism geometry. The upper square defined by O(2)O(5)O(6)O(7) has an average Gd–O distance of 2.368 Å and the lower square defined by

Table 2
Selected bond distances (Å) and angles (°) for **1** and **2**

|  | **1** (M = Cu) | **2** (M = Ni) |
|---|---|---|
| *Gd coordination sphere* | | |
| Gd–O(1) | 2.345(3) | 2.356(2) |
| Gd–O(2) | 2.420(3) | 2.391(3) |
| Gd–O(3) | 2.356(3) | 2.389(2) |
| Gd–O(4) | 2.384(3) | 2.374(2) |
| Gd–O(5) | 2.378(3) | 2.346(2) |
| Gd–O(6) | 2.363(3) | 2.353(2) |
| Gd–O(7) | 2.485(3) | 2.381(2) |
| Gd–O(8) | 2.348(3) | 2.470(2) |
| | | |
| O(1)–Gd–O(8) | 144.21(10) | 80.57(9) |
| O(1)–Gd–O(3) | 86.08(10) | 74.51(8) |
| O(8)–Gd–O(3) | 104.45(11) | 83.76(8) |
| O(1)–Gd–O(6) | 107.93(12) | 147.80(9) |
| O(8)–Gd–O(6) | 87.40(11) | 113.02(8) |
| O(3)–Gd–O(6) | 137.55(12) | 133.80(8) |
| O(1)–Gd–O(5) | 70.05(11) | 110.14(10) |
| | | |
| O(8)–Gd–O(5) | 145.40(11) | 150.17(9) |
| O(3)–Gd–O(5) | 76.46(12) | 73.16(9) |
| O(6)–Gd–O(5) | 71.68(11) | 73.15(9) |
| O(1)–Gd–O(4) | 141.37(11) | 139.57(9) |
| O(8)–Gd–O(4) | 73.42(11) | 73.86(8) |
| O(3)–Gd–O(4) | 71.30(11) | 72.05(8) |
| O(6)–Gd–O(4) | 73.60(13) | 72.29(9) |
| | | |
| O(5)–Gd–O(4) | 74.34(12) | 81.09(9) |
| O(1)–Gd–O(2) | 71.17(10) | 70.87(9) |
| O(8)–Gd–O(2) | 80.04(10) | 133.67(9) |
| O(3)–Gd–O(2) | 70.93(11) | 120.61(9) |
| O(6)–Gd–O(2) | 151.34(11) | 79.54(9) |
| O(5)–Gd–O(2) | 130.23(10) | 75.55(10) |
| O(4)–Gd–O(2) | 125.80(12) | 147.57(9) |
| | | |
| O(1)–Gd–O(7) | 91.40(9) | 92.94(9) |
| O(8)–Gd–O(7) | 63.06(9) | 59.88(7) |
| O(3)–Gd–O(7) | 151.54(11) | 143.23(8) |
| O(6)–Gd–O(7) | 69.93(10) | 71.91(8) |
| O(5)–Gd–O(7) | 129.01(11) | 142.63(9) |
| O(4)–Gd–O(7) | 123.22(10) | 100.39(8) |
| O(2)–Gd–O(7) | 81.41(10) | 85.46(9) |
| | | |
| M–N(1) | 1.917(4) | 1.853(3) |
| M–N(2) | 1.935(4) | 1.847(3) |
| M–O(7) | 1.913(3) | 1.847(2) |
| M–O(8) | 1.891(3) | 1.842(2) |
| | | |
| O(8)–M–O(7) | 83.40(12) | 82.10(10) |
| O(8)–M–N(1) | 178.29(14) | 170.40(11) |
| O(7)–M–N(1) | 94.91(14) | 93.71(11) |
| O(8)–M–N(2) | 93.11(14) | 95.90(12) |
| O(7)–M–N(2) | 171.74(17) | 177.13(11) |
| N(1)–M–N(2) | 88.60(16) | 88.58(12) |
| | | |
| *Bridging system* | | |
| Gd–M | 3.2525(5) | 3.0964(5) |
| | | |
| M–O(7)–Gd | 94.51(11) | 93.33(9) |
| M–O(8)–Gd | 99.67(12) | 90.60(9) |

Fig. 2. ORTEP diagram of complex **2**.
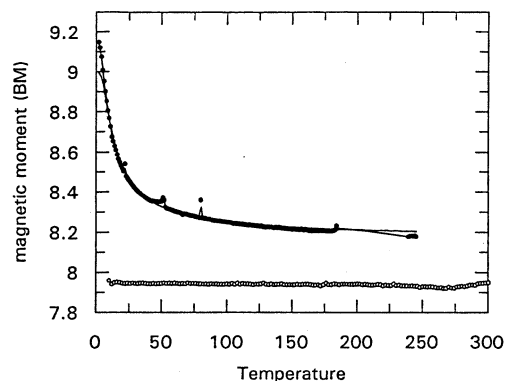


Fig. 3. Plots of $\mu_{\text{eff}}$ vs. $T$ for **1** (●) and for **2** (○).

O(1)O(3)O(4)O(8) has an average Gd–O distance of 2.397 Å. The deviations from the mean plane formed by Ni O(7) O(8) N(1) N(2) are 0.04 Å for Ni, 0.08 Å for O(7), −0.10 Å for O(8), −0.09 Å for N(1) and 0.07 Å for N(2).

The structures of **1** and **2** bear similarities to the structures reported previously of Gd(hfa)$_3$Cu(salen) and Gd(hfa)$_3$Cu(salen)(meim). The earlier structures also contain eight coordinate Gd(III) in a distorted square antiprism geometry with copper and gadolinium doubly bridged by the two O atoms of the salen Schiff base ligand. The Gd–Cu distances vary from 3.198 Å in Gd(hfa)$_3$Cu(salen) to 3.252 Å in Gd(hfa)$_3$Cu(salen)-(meim) as compared with 3.2525 Å in **1**. The bridging network is likewise bent with dihedral angles between the O Gd O and O Cu O planes of 133.0 and 140.43° for Gd(hfa)$_3$Cu(salen) and Gd(hfa)$_3$Cu(salen)(meim), respectively, compared with a value of 137.8° for **1**. Cu(II) is four coordinate in Gd(hfa)$_3$Cu(salen) and in **1**, and five coordinate in Gd(hfa)$_3$Cu(salen)(meim). For Gd(hfa)$_3$Cu(salen), in which salen is substituted for the prpen ligand of **1**, the complex crystallizes in dimeric units with an intermolecular Cu–Cu distance of 3.630 Å. In its previously reported dinuclear complexes [4], as well as the Gd–Cu dinuclear reported here, Cu(prpen) shows no such tendency toward dimerization. In **1** the shortest distance between neighboring Cu(II) ions is 4.103 Å, significantly longer than that observed in Cusalen–Gd(hfa)$_3$, and the shortest distance between Cu and a phenolato O of a neighboring Cuprpen unit is 4.007 Å.

### 3.2. Magnetism of 1 and 2

The magnetic behavior of **1** and **2** is represented in Fig. 3 in the form of the plot of $\mu_{\text{eff}}$ versus $T$. The magnetic data for **1** clearly indicates ferromagnetism. The experimental data were fitted (solid line in Fig. 3) using the theoretical expression for $\chi_M$:

$$\chi = \frac{Ng^2\beta^2}{kT} \cdot \frac{(28 + 60e^{4J/kT})}{(7 + 9e^{4J/kT})} + N_\alpha$$

in which $g$ is the gyromagnetic ratio, $\beta$ is the Bohr Magneton, $k$ is Boltzman's constant, and $N_\alpha$ is the temperature independent paramagnetism, which is estimated to be $1.00 \times 10^{-4}$ cm$^3$ mol$^{-1}$. The low temperature, ferromagnetic limit for $\mu_{\text{eff}}$ is 8.94 BM and the high temperature limit, calculated for noninteracting $S = 7/2$ and $S = 1/2$ metals, is 8.12 BM. Values of $g$ and the coupling constant, $J$, were determined by nonlinear regression analysis and were found to be 2.0461(0.0006) and 1.91(0.03) cm$^{-1}$, respectively. Previous correlations of diphenolato-bridged Gd(III)–Cu(II) dinuclear complexes support the expectation that the strength of the magnetic coupling increases with planarity of the Gd–O$_2$–Cu bridging framework [13]. A $J$ value of 1.91 cm$^{-1}$ for **1** is similar to that reported for Gd(hfa)$_3$Cusalen(1-MeIm) ($J = 1.42$ cm$^{-1}$), consistent with the similar and significant distortions from planarity of their bridging networks. For comparison, a nearly planar bridging system (a dihedral angle of 178.4° between the OGdO and OCuO planes of the Gd–O$_2$–Cu framework) was reported for a Gd(III)–Cu(II) dinuclear with a $J$ value of 10.1 cm$^{-1}$ [13].

For complex **2**, the Ni(II) ion is in a square planar ligand set and has $S = 0$. An effective magnetic moment, $\mu_{\text{eff}}$, of 7.95 $\mu_B$ at 300 K which remains relatively constant down to 10 K is consistent with an isolated Gd(III) ($S = 7/2$) ion.

### 3.3. Gd(hfa)$_3$ Ni(L) (3)

Complex **3** formed a crystalline powder, but no crystals large enough to attempt an X-ray study. As with the symmetrical Schiff base complexes, Cuprpen and Niprpen, NiL forms a dinuclear with Gd(hfa)$_3$. Unlike the symmetrical complexes, we propose that the dinuclear Gd(hfa)$_3$NiL is bridged via imidazolate rather than phenolate. NiL differs from the symmetrical complexes in having only one phenolate O atom and so is

incapable of forming the doubly bridged structure seen in the dinuclears of M(prpen) with Gd(hfa)$_3$. However, it has the outer nitrogen of the imidazolate ring available for bridging to Gd(hfa)$_3$. In addition, the imidazolate N is better able to bind to Gd(hfa)$_3$ than the phenolate O of NiL because it is sterically more accessible. These same arguments have been used to explain imidazolate bridging in dinuclears formed by Cu(CBP-PHEN-Im) and M(hfa)$_2$ {M = Co(II), Cu(II)} [14]. H$_2$(CBP-PHEN-Im) is a close relative of H$_2$L, differing only in the absence of a methyl group on the imidazole ring.

The Gd(III)–Ni(II) complex **3** prepared in this study is only the second example reported of a Gd(III)–M(d block) complex for which imidazolate bridging between Gd(III) and M(II) is likely. A Gd(III)–Cu(II) dinuclear is reported by Sakamoto [3] to contain a bridging imidazolate ligand, but no structural investigation of the complex has been published. As in the present study, the formulation of the complex is based on elemental analysis data. While Gd(III) generally shows an affinity for O donors, it does form stable complexes with some N donors [15–17]. Furthermore, the reactivity of Gd(hfa)$_3$ toward an imidazolate donor was demonstrated using Fetren(meim)$_3$, which has been shown to bind M(hfa)$_2$ {M = Cu(II), Ni(II)} via one of three possible imidazolate sites [18]. With Gd(hfa)$_3$, Fetren(meim)$_3$ in CHCl$_3$ solution underwent an immediate color change from red to blue with the formation of a solid precipitate. Analysis of the solid by IR revealed the presence of hfa in the product.

The syntheses reported in this work are part of a broad effort to prepare dinuclears of lanthanide ions and transition metals, in particular, Gd(III) and Cu(II), with a variety of bridging ligands. The commonly held expectation is that the Gd(III)–Cu(II) interaction will be ferromagnetic regardless of structure. In fact, this prediction has been upheld by all but one of the structurally and magnetically characterized dinuclear complexes reported thus far, as well as the complex reported in this work. However, in light of a recent example of an antiferromagnetically coupled Gd(III)–Cu(II) complex, renewed effort at preparing Gd(III)–Cu(II) dinuclears, with the particular aim of expanding the examples of bridging systems to include unsymmetric, and non-O atom donors, is warranted.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154522 for compound **1** and CCDC No. 154523 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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