Expanding the 3d–4f heterometallic chemistry of the (py)$_2$CO and pyCOpyCOpy ligands: structural, magnetic and Mössbauer spectroscopic studies of two Fe$^{II}$–Gd$^{III}$ complexes†

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Complex [Fe$^{II}$Gd$^{III}$]([pyCO(OEt)pyCOH(OEt)py])$_3$(ClO$_4$)$_2$ (I) crystallizes in the Cc space group and contains one hexacoordinate ferrous ion and one enneacoordinate Gd$^{III}$ ion. Complex [Fe$^{II}$,Gd$^{III}$]([pyCO(OEt)pyC(OH)(OEt)py])$_3$(ClO$_4$)$_2$ (II) crystallizes in the C2/c space group and contains two hexacoordinate ferrous ions and one octacoordinate Gd$^{III}$ ion. Both complexes have been prepared by the metal-assisted ethanolysis of ligands di-2,6-(2-pyridylcarbonyl)pyridine (pyCOpyCOpy, dpcp; Scheme 1), which exhibit similar structures.

Mössbauer spectroscopic studies of 2 revealed the presence of two quadrupole-split doublets of equal intensities, each assigned to a ferrous site. These doublets exhibit similar isomer shifts ($\delta_i = 1.11$ mm s$^{-1}$, $\delta_j = 1.11$ mm s$^{-1}$) but quite different quadrupole splittings ($\Delta E_Q = 3.55$ mm s$^{-1}$, $\Delta E_Q = 2.74$ mm s$^{-1}$). Magnetic studies revealed weak ferromagnetic Fe$^{II}$–Gd$^{III}$ interactions for both complexes ($J_{FeGd} = +0.68$ cm$^{-1}$, $D_{0G} = 12.0$ cm$^{-1}$ for I and $J_{FeGd} = +0.03$ cm$^{-1}$, $J_{FeF} = -1.73$ cm$^{-1}$ for 2, according to the -$J_{S_S},S_i$ spin-Hamiltonian formalism).

Introduction

The heterometallic 3d–4f chemistry of metal clusters has received considerable attention in recent years as it has been proposed that the combination of paramagnetic 3d ions with highly anisotropic trivalent lanthanides may lead to polynuclear complexes exhibiting ground states of high magnetic moments and anisotropies. Moreover, the problem of magnetic exchange between transition metals and lanthanides is significant in itself; theoretical models are still under development to gain a better understanding of the parameters that govern 3d–4f magnetic exchange. Gd$^{III}$, being the only paramagnetic Ln$^{III}$ ion without orbital contributions, allows a straightforward interpretation of its magnetic properties through the spin Hamiltonian approach. For this reason, most studies addressing this problem have been carried out on M–Gd$^{III}$ complexes. Of those complexes, the large majority contain Cu$^{II}$ as its 3d ion. 1 Magnetic studies of M–Gd$^{III}$ complexes with other transition metals, e.g. high-spin Ni$^{III}$, Mn$^{II}$, Co$^{II}$, Fe$^{III}$ also exist, but are less numerous. Being interested in the chemistry and magnetic properties of Fe$^{II}$ complexes, we had noticed that only a handful of Fe$^{II}$–Gd$^{III}$ complexes have been studied magnetically. To the best of our knowledge these examples are restricted to work carried out by Costes et al. 7 and in all cases have revealed ferromagnetic Fe$^{II}$–Gd$^{III}$ interactions.

We therefore considered it of interest to expand the known Fe$^{II}$–Gd$^{III}$ chemistry to include new complexes. On the one hand, this might be a promising pathway to clusters with high magnetic anisotropies, or even Single-Molecule Magnets; this might be possible not only due to the high magnetic anisotropies of paramagnetic Ln$^{III}$ ions (Ln$^{III}$ ≠ Gd$^{III}$), but also due to the high magnetic anisotropy of iron(II), which has recently been calculated to reach even 50 cm$^{-1}$. On the other hand, such new examples of Fe$^{II}$–Gd$^{III}$ complexes may help us reach a better understanding of the Fe$^{II}$–Gd$^{III}$ magnetic interaction.

The study of the heterometallic M$^{II}$–Gd$^{III}$ chemistries of di-2,6-(2-pyridylcarbonyl)pyridine (pyCOpyCOpy, dpcc, Scheme 1) and its parent ligand, di-2-pyridyl ketone ((py)$_2$CO, dpk, Scheme 1), has previously been initiated to examine the magnetic properties of the derived complexes. In particular, using the ligand dpcc, we were able to isomorphously replace several M$^{II}$ ions (M$^{II}$ = Cu$^{II}$, Mn$^{II}$, Ni$^{II}$, Co$^{II}$ and Zn$^{II}$) in the [M$^{II}$Gd$^{III}$]([pyCO(OEt)pyCOH(OEt)py])$_3$(ClO$_4$)$_2$ cluster type and study the magnetic interactions of different paramagnetic ions with Gd$^{III}$. In related work, some of us (A. N. G and C. P. R.) were involved in the preparation of a se-
of trinuclear cationic complexes with the general formula [Ni_{ii}M_{ii}'{(py)_{2}CO(OEt)}_{3}]_{2}{[(py)_{2}CO(OR)(NO)_{3}(H_{2}O)]}A_{0.5}(ClO_{4}) \ (M_{ii}'=Tb_{ii}, \ Gd_{ii}; \ A^{-}=ClO_{4}^{-} \ and \ R=H; \ M_{ii}=Y_{iii}, \ Dy_{iii}; \ A^{-}=0.5[M'(NO_{3})_{3}]^{2-} \ and \ R=Et).^{9}

The above mentioned work with dpcp,\(^{2}\) illustrating the isomorphous replacement of a series of several divalent 3d metal ions in a controlled manner within a structural type, suggested the possibility of preparing the respective Fe^{ii} complex. Moreover, previous work with dpk, which revealed that enneanuclear complexes of the structural type [M^{ii}_{9}(X)_{4}((py)_{2}CO)_{3}O(OCMe)_{6}] can be obtained reproducibly for M^{ii} = Co^{ii}, Ni^{ii} and Fe^{ii} \(^{5}\) (X' = OH', N_{3}^{-} and NCO^{-}), suggested that these three metal ions can behave in a similar manner in the formation of clusters (in anaerobic conditions in the case of Fe^{ii}). We consequently considered the possibility of preparing the \([Fe^{ii}Gd^{iii}]\) analogue of the \([Ni^{iii},M^{ii}]\) complexes previously reported.\(^{9}\)

Herein, we report the preparation of two complexes, \([Fe^{ii}Gd^{iii}\{(py)CO(OEt)pyCOH(OEt)py\}](ClO_{4})\) \(1\) and \([Fe^{ii}-Gd^{iii}\{(py)CO(OEt)py\}(NO)_{3}(H_{2}O)](Gd(NO_{3})_{3})_{0.5}(ClO_{4})\) \(2\), obtained by substituting M^{ii} = Fe^{ii} in the previously described synthetic procedures. We also report on the magnetic properties of these complexes and the Mössbauer spectroscopic properties of complex 2.

**Results and discussion**

**Syntheses**

The reactions leading to both complexes proceed by metal-assisted ethanolysis of the carbonyl carbon atom.

The reaction leading to \(1\) can be summarized in eqn (1):

\[
\begin{align*}
2 \text{Fe(ClO}_4)_2 \cdot 6\text{H}_2\text{O} + 2 \text{py}_2\text{CO} + 1.5 \text{Gd(NO}_3)_3 \cdot 6\text{H}_2\text{O} + 4 \text{EtOH} \rightarrow \\
[\text{FeGd(pyCO(OEt)pyCOH(OEt)py}]_3(\text{ClO}_4)_2 \ (1)
\end{align*}
\]

The reaction leading to \(2\) can be summarized in eqn (2).

\[
\begin{align*}
\text{Scheme 1} \quad \text{Ligands dpk (}(py)_2\text{CO, dpk)}
\end{align*}
\]
Description of the structures

A POV-Ray plot of the cation of complex 1 is shown in Fig. 1. The complex is isostructural to the series of complexes previously described, so its structure will not be analyzed in detail. We only note that the Fe atom in the complexes is hexacoordinate, adopting a geometry intermediate between octahedral and trigonal prismatic, with Fe–L distances ranging from 2.077(3) to 2.154(4) Å, characteristic of high-spin FeII species. These are consistently longer than the bonds of the respective MnII complex and consistently shorter than those of the respective NiII complex.

The Gd atoms are enneacoordinate. Bridging is achieved by three monatomic alkoxo bridges belonging to the three dpcp ligands, with the Fe–O–Gd angles varying between 84.57(10) and 85.14(11)°.

The dpcp ligand is present in its singly deprotonated \( \{pyC(O)(OEt)pyC(OH)(OEt)py\}^- \) form, having undergone ethanolysis on both its carbonyl atoms. One pyridyl ring of each ligand molecule is coordinated to the Fe atom, another to the Gd atom, while the third is non-coordinated. This latter pyridyl ring participates, via its N-atom, in H-bonding with the protonated hydroxyl group of an adjacent ligand molecule.

A POV-Ray plot of the cation of complex 2 is shown in Fig. 2. The structure of this complex is similar to the structures of the previously reported NiII–GdIII complexes. In our case, however, instead of two perchlorate counteranions per cluster, the charge balance is maintained by one perchlorate and half a \([\text{Gd(NO}_3\text{)]}^2-\) anion shared between two symmetry-related cations, the latter being situated on a two-fold crystallographic axis.

The Fe atoms exhibit a coordination geometry intermediate between octahedral and trigonal prismatic. Similarly with above, we compare the Fe–L distances to those of the respective NiII complex; in this case, the Fe–L distances (ranging between 2.014(6)–2.298(6) Å) are comparable to the respective distances of the NiII complex (ranging between 2.012–2.218 Å).

Mössbauer spectroscopy

Due to the small yield of the reaction and the limited quantity of dpcp available, a sufficient quantity of complex 1 could not be isolated to conduct Mössbauer spectroscopic studies. This was only possible in the case of 2.

The 80 K Mössbauer spectrum of 2 is shown in Fig. 3. It consists of two well-resolved, symmetric, quadrupole-split doublets of equal intensities, with parameters typical of high-spin iron(II) in octahedral N/O environments. These doublets were fitted to two nested Lorentzians, taking into consideration that the isomer shifts are mostly affected by the donor-atom types, which in the current case are identical for both sites. Best-fit parameters according to this model were \( \delta_1 = 1.14 \text{ mm s}^{-1}, \Delta E_{Q1} = 3.55 \text{ mm s}^{-1}, \Gamma_{1/2(1)} = 0.14 \text{ mm s}^{-1} \) and \( \delta_2 = 1.11 \text{ mm s}^{-1}, \Delta E_{Q2} = 2.74 \text{ mm s}^{-1}, \Gamma_{1/2(2)} = 0.13 \text{ mm s}^{-1} \).

These results are in agreement with the crystal structure of 2 which reveals the presence of two similar, but not crystallographically equivalent, iron atoms. Fe(1) and Fe(2) both exhibit similar N3O3 coordination spheres, however they are not identical. These ferrous sites give rise to two distinct quadrupole-split doublets due to the tendency of iron(II) to exhibit important variations in its Mössbauer parameters, even for small variations of its ligand-field geometries. It is noteworthy that both doublets are quite narrow, suggesting very well-defined and uniform local geometries for both ferrous sites.

From these data alone, however, we are not able to distinguish the contribution of each ferrous site to the Mössbauer spectrum. The geometric parameters of each coordination sphere vary within...
comparable ranges; e.g., the bond lengths of Fe(1) and Fe(2) vary within 0.285 Å (2.014(6)–2.298(6) Å) and 0.170 Å (2.071(5)–2.242(7) Å), respectively and the average deviation of the trans L–Fe–L angles from 180° is 21.7° and 25.2°, respectively. Therefore, we cannot make a meaningful assignment of each doublet to a particular site.

Magnetic properties

The magnetic properties of complexes 1 and 2 were studied using dc and ac magnetic susceptibility. Their variable-temperature data are shown in Fig. 4 and variable-field magnetization data are shown in Fig. 5. For the interpretation of the data the spin-Hamiltonian approach was undertaken. We should note that as octahedral FeII has an orbitally degenerate \(^5T_g\) ground state, the spin-Hamiltonian is an approximation, assuming important distortions around FeII.\(^{12}\)

[Image 48x343 to 283x518]

**Fig. 4** \(\chi_M T\) vs. \(T\) data for 1 (dc data) and 2 (ac data under zero applied field) and theoretical curves from the best-fit parameters according to the models described in the text. The data of 2 have been corrected for the paramagnetic contribution of the [Gd(NO\(_3\)]\(^3+\) counteranion.

Complex 1. The \(\chi_M T\) value at 300 K for 1 is 10.92 cm\(^3\) mol\(^{-1}\) K at 0.1 T, very close to the value predicted for one Fe\(^{III}\) and one Gd\(^{III}\) ion without magnetic interactions (10.88 cm\(^3\) mol\(^{-1}\) K, \(g_{Fe} = g_{Gd} = 2\), suggesting very weak interactions. This remains practically constant upon cooling down to 100 K, below which temperature it increases, reaching 12.61 cm\(^3\) mol\(^{-1}\) K at 7 K, thus suggesting ferromagnetic interactions. Further cooling leads to a decrease of the \(\chi_M T\) value, reaching 11.33 cm\(^3\) mol\(^{-1}\) K at 2 K, probably due to the combined effects of Zeeman and zero-field splitting interactions and possibly intermolecular interactions.

Given the strictly dinuclear structure of the complex, a simple isotropic-exchange spin-Hamiltonian could be employed for the interpretation of its magnetic properties. However, since the single-ion zero-field splitting (zfs) cannot be considered negligible for iron(II), a zfs parameter, \(D_{Fe}\), was also considered. The corresponding Hamiltonian was:

\[
\hat{H} = -J_{FeGd} \hat{S}_{Fe} \hat{S}_{Gd} + D_{Fe} \hat{S}_{Fe}^z + \beta g_{Fe} H (\hat{S}_{Fe}^+ + \hat{S}_{Fe}^-) \tag{3}
\]

Best-fit parameters according to this model were \(J_{FeGd} = +0.68\) cm\(^{-1}\), \(D_{Fe} = 12.0\) cm\(^{-1}\), \(g = 1.99\) \((R = 5.4 \times 10^{-6})\). Fitting attempts with \(D_{Fe} < 0\) invariably failed to give satisfactory results. The weak ferromagnetism in 1 is in agreement with previously explored systems.\(^7\) It should be noted that \(g\) is taken as a global fitting parameter, therefore its value does not reflect the values of the individual \(g_{Fe}\) and \(g_{Gd}\) parameters, which are expected to be quite different.

Magnetization isothermal studies at 2 K revealed the onset of saturation above ~5 T, at 10.30 \((N_{A} \mu_B)\). Excellent simulations were obtained with the \(J\) and \(g\) parameters derived from the fits to the magnetic susceptibility data, and \(D_{Fe} = +8\) cm\(^{-1}\).

Zero-field ac magnetic susceptibility experiments carried out on 1 down to 2 K did not reveal any out-of-phase signals for frequencies between \(10^{-1}–10^{6}\) Hz, thus precluding magnetic relaxation phenomena at the corresponding timescales.

Complex 2. A complication arising in the interpretation of the magnetic properties of 2 is the presence of the paramagnetic counteranion [Gd(NO\(_3\)]\(^3+\), whose contribution at low temperatures is expected to deviate from that of a simple Curie paramagnet due to Zeeman interactions inside a magnetic field. This was circumvented by carrying out magnetic susceptibility studies on 2 using ac susceptibility under zero magnetic field. We were thus able to consider a simple Curie behavior for [Gd(NO\(_3\)]\(^3+\), and account for it by simple subtraction of its theoretical contribution from the \(\chi_M T\) vs. \(T\) data (3.94 cm\(^3\) mol\(^{-1}\) K, considering \(g = 2\) and counting half a counteranion per cluster). These corrected data were used for subsequent interpretation and are described below.

The corrected \(\chi_M T\) product at 300 K is 13.59 cm\(^3\) mol\(^{-1}\) K for 2, in agreement with the value predicted for one Gd\(^{III}\) and two Fe\(^{II}\) non-interacting ions (13.87 cm\(^3\) mol\(^{-1}\) K), suggesting very weak interactions. This is corroborated by its thermal behavior, as it remains almost constant upon cooling down to 100 K. It then decreases more rapidly, reaching a value of 8.44 cm\(^3\) mol\(^{-1}\) K at 2 K.

Taking into account the crystal structure of the cation of 2, revealing two inequivalent ferrous sites, a rigorous interpretation of its magnetic properties would require the consideration of three isotropic exchange interactions: two between each ferrous ion and the Gd\(^{III}\) ion (\(J_{FeGd}\) and \(J_{FeGd}\)) and one between the two ferrous ions. Moreover, iron(II) being known to exhibit important
axial zero-field-splitting (zfs), two different axial zfs parameters ($D_{\text{Fe1}}$ and $D_{\text{Fe2}}$) would also be required. Indeed, as we have previously shown, small structural distortions in ferrous sites give rise to quite different zfs parameters.\(^6\) However, in order to avoid overparametrization, we initially employed a simpler model, with $J = J_{\text{FeGd}} = J_{\text{FeFe}}$, $J = J_{\text{FeGd}}$ and $D = D_{\text{Fe1}} = D_{\text{Fe2}}$. Therefore, the spin Hamiltonian employed was:

$$
\hat{H} = -J_{\text{FeGd}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Gd}} + \hat{S}_{\text{Fe2}} \cdot \hat{S}_{\text{Gd}}) - J_{\text{FeFe}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}}) + D_{\text{Fe1}} S_{z, \text{Fe1}} + D_{\text{Fe2}} S_{z, \text{Fe2}}
$$

(4)

Initial attempts fixing $D_{\text{Fe}} = 0$ yielded best-fit parameters $J_{\text{FeGd}} = +0.03\text{ cm}^{-1}$, $J_{\text{FeFe}} = -1.73\text{ cm}^{-1}$, $g = 1.98$ ($R = 2.7 \times 10^{-4}$, solution A). The fit was of high quality, suggesting that liberation of the $D_{\text{Fe}}$ parameter might lead to overparametrization. Indeed, doing so yielded fits of comparable quality and similar parameters, suggesting that inclusion of additional variables in this model may not be meaningful. The uniqueness of this solution for a $2J$ model was also tested by error contour-plots, which confirmed this solution as the sole minimum of the error function (Figure S4, ESI†).

However, considering the very small value of $J_{\text{FeGd}}$, we also wondered whether acceptable fits might be possible by fixing this parameter to zero. A model considering $J_{\text{FeGd}} = 0$ yielded best-fit parameters $J_{\text{FeFe}} = -1.59\text{ cm}^{-1}$, $g = 1.98$ ($R = 2.8 \times 10^{-4}$, solution B), very close in quality to the previous one.

Solutions A and B deserve some further comment: the magnetic couplings observed in 1 and in the complexes reported by Costes et al.\(^7\) indicate that some Fe\(\text{II}\)–Gd\(\text{III}\) magnetic coupling, albeit weak, might reasonably be expected for 2. The existence of a high-quality fitting solution with $J_{\text{FeGd}} = 0$ does not necessarily preclude the presence of such an interaction; it may instead be interpreted as an indeterminacy of this weak interaction, in the presence of the stronger and competing Fe\(\text{II}\)–Fe\(\text{II}\) interaction within this spin-frustrated system. It is, however, useful to note that when the $J_{\text{FeGd}}$ was liberated it invariably assumed positive values, suggesting that this interaction, if indeed operative, is most probably ferromagnetic.

Magnetization isotherms were collected for 2 at 2 K and were corrected for the contribution of the paramagnetic [Gd(NO$_3$)$_3$]$^{3-}$ counteranion (for which a Brillouin behaviour was assumed, $g = 2$). These did not reveal the onset of saturation, even at 9 T, suggesting the presence of low-lying excited states, in accordance with weak exchange couplings. Satisfactory simulations were obtained with the parameters from solution A and by assuming $D_{\text{Fe}} = +12\text{ cm}^{-1}$, common for both iron(II) ions. Attempts to simulate the data with $D_{\text{Fe}} < 0$ did not yield satisfactory results.

Like in the case of 1, the ac experiments of 2 did not reveal any out-of-phase signals down to 2 K for frequencies between 10$^1$–10$^4$ Hz, thus precluding magnetic relaxation phenomena at the corresponding timescales.

General comments regarding the magnetic properties of 1 and 2. The magnetic exchange parameters derived for 1 and 2 are in agreement with previously reported data (see Table 1), showing weak ferromagnetic interactions in all cases. In particular, the $J_{\text{FeGd}}$ parameter of 1 (0.68 cm$^{-1}$) falls well within the range previously reported (0.16–1.00 cm$^{-1}$), while that of 2, if allowed to vary, is below the low end of that range. Complex 2 may be directly compared to complex IV which also contains a trinuclear Fe\(\text{II}\)–Gd\(\text{III}\) core. However, in the case of IV, the lack of any significant Fe–Fe magnetic interaction allows for a more accurate determination of $J_{\text{FeGd}}$ and $D_{\text{Fe}}$, since the presence of $J_{\text{FeGd}}$ in 2 increases the correlations between variables and the uncertainties in their determination. Nevertheless, our statistical analysis and various tests reliably show that $J_{\text{FeGd}}$ in 2 is most probably ferromagnetic and quite weak.

Conclusions

From a synthetic perspective, in this work we were able to add two new members to the small family of structurally and magnetically studied Fe\(\text{II}\)–Gd\(\text{III}\) clusters. In doing so, we were also able to prepare the sixth member of the [M\(\text{II}\)Gd\(\text{III}\)(pyCO(OEt)pyC(OH)(OEt)py)$_2$]ClO$_4$ family of complexes, now including all M\(\text{II}\) ions between Mn\(\text{II}\) and Zn\(\text{II}\) from the fourth row of the periodic table. Having further established the stability of this structural type, we are interested in seeing whether additional analogues can be prepared with M\(\text{II}\) ions of the fifth or sixth rows, i.e. 4d and 5d elements. Such experiments, if successful, should allow us to study the magnetic properties of 4d–4f and 5d–4f complexes, also a topic of current interest. Moreover, the preparation of the ferrous analogue of the [M\(\text{II}\)M\(\text{III}\)(py)$_2$CO(OEt)$_2$]ClO$_4$ structural type (M\(\text{III}\) = Y\(\text{III}\), Ln\(\text{III}\); R = H, Et), suggests the M\(\text{II}\) replacement as a new synthetic perspective for this system.

From a magnetic perspective, we were able to increase the known examples of magnetic exchange between Fe\(\text{II}\) and Gd\(\text{III}\), previously limited to only four.\(^7\) Like in previous studies, this magnetic exchange was found to be weakly ferromagnetic. This was not directly assigned to structural factors, but considered as the combined result of such factors and the anisotropy of the ferrous ions. However, for a better understanding of the

Table 1. $J$ and $D$ values for Fe\(\text{II}\)–Gd\(\text{III}\) complexes reported in the literature (I–IV) and in the present work (1, 2)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{\text{FeGd}}$ (cm$^{-1}$, -JS,S formalism)</th>
<th>$D$ (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[L(\text{II})Fe(MeOH)Gd(NO$_3$)$_3$(MeOH)$_3$] (I)</td>
<td>1.00</td>
<td>2.06</td>
<td>7a</td>
</tr>
<tr>
<td>[L(\text{II})Fe(Me$_2$CO)Gd(NO$_3$)$_3$] (II)</td>
<td>0.82</td>
<td>3.22</td>
<td>7a</td>
</tr>
<tr>
<td>[L(\text{II})Fe(MeCO)Gd(NO$_3$)$_3$] (III)</td>
<td>0.16</td>
<td>4.43</td>
<td>7a</td>
</tr>
<tr>
<td>[L(\text{II})FeGdFeL]ClO$_4$ (IV)</td>
<td>0.69</td>
<td>5.7</td>
<td>7b</td>
</tr>
<tr>
<td>1</td>
<td>0.68</td>
<td>8$^*</td>
<td>present work</td>
</tr>
<tr>
<td>2</td>
<td>0.03$^*$</td>
<td>12$^*</td>
<td>present work</td>
</tr>
</tbody>
</table>

* Indicative value. $^*$ Values derived from simulations to isothermal magnetization data.
FeIII-GdIII magnetic exchange mechanism, magnetic studies on similar additional complexes are required.

Experimental

Syntheses

All reagents were of analytical grade and used as received except dpdp, which was synthesized according to a literature procedure. The preparation of the complexes was carried out under anaerobic conditions inside a glovebox (MBrabn Labmaster) under a N2 atmosphere. The O2 content of the atmosphere was kept below 1 ppm by purification through a CuO column. Solvents, of analytical quality, were deoxygenated on a Schlenk line through multiple vacuum/nitrogen cycles and introduced into the glovebox without further purification. The nitrogen stream of the Schlenk line was purified through a MnO column to remove any O2 traces.

The synthesis was similar to the previous one. Solid dpdp (17.3 mg, 0.059 mmol) and NaOAc (4.5 mg, 0.033 mmol) were added to a light yellow solution of Fe(ClO4)2 (107 mg, 0.037 mmol) in EtOH (25 mL). The solution changed to light yellow-brown. After cooling, the solution was left for slow evaporation. Orange prisms of 1 formed after 1 week, which were filtered off and dried in vacuo. The yield was ~5 mg (~33% with respect to Gd(NO3)3·6H2O). The dried complex analyzed as solvent-free. Elemental analysis calculated for Cu5H35Cl2FeGdN25O56: C 48.72, H 4.28, N 8.12. Found C 48.61, H 4.19, N 8.18%. IR (KBr disk, cm−1): v = 3507 (sb) [v(=OH)]; 2975 (s) vC–H; 2875 (m) vC–=O; 1600 (s), 1574 (s), 1472 (w), 1455 (s) and 1434 (s) [v(C–C) + v(C–N)]; 1299 (w), 1270 (m), 1230 (m) and 1206 (m) δ(C–H); 1114 (w), 1066 (w) and 1051 (w) [v(C–O)py]; 991 (s) [v(F2)(ClO4)]; 914 (s) and 862 (s) [v(F2)(ClO4)]; 827 (s) and 763 (s) [π(C–H)]; 501 (sb) 

Table 2 Crystal data for complexes 1·EtOH and 2·1.3EtOH·1.3H2O

<table>
<thead>
<tr>
<th></th>
<th>1·EtOH</th>
<th>2·1.3EtOH·1.3H2O</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C23H23Cl2FeGdN25O56·EtOH</td>
<td>C23H23Cl2FeGdN25O56·EtOH·1.3EtOH·1.3H2O</td>
</tr>
<tr>
<td>FW</td>
<td>1599.32</td>
<td>1599.32</td>
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<tr>
<td>T/K</td>
<td>180(2)</td>
<td>180(2)</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 (Cu-Kα)</td>
<td>1.54178 (Cu-Kα)</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Cc</td>
<td>Cc</td>
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<tr>
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<td>15.2861(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>20.4783(3)</td>
<td>20.4783(3)</td>
</tr>
<tr>
<td>c (Å)</td>
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<td>15.2861(2)</td>
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<tr>
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<td>90</td>
</tr>
<tr>
<td>β (°)</td>
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<td>105.574(1)</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>(Å)</td>
<td>6871.89(18)</td>
<td>6871.89(18)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ (g cm−3)</td>
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</tr>
<tr>
<td>μ (mm−1)</td>
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</tr>
<tr>
<td>R1, wR2 (all)</td>
<td>1.0474</td>
<td>1.0474</td>
</tr>
<tr>
<td>R1, wR2 (obs)</td>
<td>0.1187</td>
<td>0.1187</td>
</tr>
<tr>
<td>(Δρ)max/(Δρ)min (e Å−3)</td>
<td>2.591/−1.882</td>
<td>2.591/−1.882</td>
</tr>
</tbody>
</table>

Note: *w = 1/[σ(Fi±)+aP] and P = (max(Fi±0)+2Fi)/3; R1 = Σ|Fo|−|Fc|/Σ|Fo| and wR2 = [Σ[w(Fi±–Fi)2]/Σ[w(Fi±)2]]^{1/2}
were carried out with the MAGPACK program versus H

X-ray crystallography

A yellow-orange crystal of 1 (0.62 × 0.25 × 0.20 mm) and an orange crystal of 2 (0.28 × 0.07 × 0.05 mm) were taken directly from the mother liquor and immediately cooled to 180 and 160 K, respectively. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Cu-Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program package. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F² with SHELXL-97. Crystal data collection and refinement parameters of 1 and 2 are collected in Table 2.

Physical measurements

Elemental analysis for carbon, hydrogen, and nitrogen was performed on a PerkinElmer 2400/II automatic analyzer. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm⁻¹ on a Bruker Equinox 55/S FT-IR spectrophotometer. Mössbauer spectra were collected with a constant acceleration spectrometer using a ⁵⁷Co (Rh) source at RT and a variable-temperature Oxford cryostat. To avoid sample oxidation, the Mössbauer sample holders were sealed with araldite glue inside the glovebox. Variable-temperature dc magnetic susceptibility data of 1 were collected on a Quantum Design MPMS SQUID susceptometer operating under a magnetic field of 0.1 T and variable-temperature ac data of 2 were collected on a Quantum Design PPMS. To avoid sample oxidation during sample transfer, the samples were loaded into gelatine capsules, mounted on plastic straws inside the glovebox and transferred to the magnetometers immersed in liquid nitrogen. Diamagnetic corrections for the complexes were estimated from Pascal’s constants. The magnetic susceptibilities were computed by analytical expressions derived as described in the text (for 1) and by exact calculation of the energy levels associated with the spin Hamiltonian through diagonalization of the full matrix with the enhanced version of a general program for axial symmetry (for 1 and 2). Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT. The error-factor R is defined as 

\[ R = \frac{1}{N} \sum \frac{(\chi_{\text{exp}} - \chi_{\text{calc}})^2}{\chi_{\text{exp}}^2} \]

where N is the number of experimental points. Simulations of M versus H were carried out with the MAGPACK program package.

Acknowledgements

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References

2 A. N. Georgopoulou, R. Adam, C. P. Raptopoulou, V Psycharis, R. Ballesteros, B. Abarca and A. K. Boudalis, Dalton Trans., 2010, 39, 5020. See also correction (Dalton Trans., 2010, 39, 11680) and references regarding Ni²⁺, Mn²⁺ and Co³⁺ complexes of Gd⁶⁺.
6 A. K. Boudalis, J. M. Clemente-Juan, F. Dahan, J.-P. Tuchagues, Inorg. Chem., 2004, 43, 1574–1586 For the subtle effects of geometrical distortions on the single-ion Dq parameter see complex 3 of that work; for similar effects on quadrupole splittings see complexes 1 and 5–7.
12 From a purely geometric perspective, this assumption has been found to be fulfilled to various extents, mostly in the case of 2, with the Fe atoms exhibiting distortions towards trigonal prismatic geometries (see ESIF). However, these geometric criteria cannot discern the influence of the donor atom types (all iron atoms possess N,O chrophores), which will tend to lower the symmetry of the coordination sphere. These two factors cause significant departures from ideal octahedral geometry.