Synthesis and characterization of dodecahedral cerium(IV) and gadolinium(III) complexes with a tetradentate Schiff Base

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Abstract. Reactions of $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with biacetyl bis(benzoylhydrazone) (H_2babh) and KOH in 1:2:2 mole ratio in methanol afford the complexes $[\text{Ce}(\text{babh})_2]$ (**1**) and $[\text{Gd}(\text{babh})(\text{Hbabh})] \cdot \text{H}_2\text{O}$ (**2**· H_2O), respectively in good yields. Characterization of the complexes has been performed with the help of elemental analysis, magnetic susceptibility, spectroscopic (IR, UV-Vis, EPR and NMR) and X-ray crystallographic measurements. **1** is diamagnetic and NMR active, while **2**· H_2O is paramagnetic ($\mu_{\text{eff}} = 8.03 \mu_{\text{B}}$ at 300 K) and EPR active. The complexes crystallize as **1**· CH_2Cl_2 and **2**· H_2O . X-ray structures show that the metal centre in each of **1** and **2** is in a distorted dodecahedral N_4O_4 coordination sphere assembled by two meridionally spanning ONNO-donor ligands. Self-assembly of **1**· CH_2Cl_2 via intermolecular $\text{C}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{Cl}$ hydrogen bonds and $\pi-\pi$ interactions provides one-dimensional ‘ladder’ type structure. On the other hand, **2**· H_2O assembles into a two-dimensional ‘sheet’ like network through intermolecular $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds.

Keywords. Cerium(IV); Gadolinium(III); Tetradentate ligand; Dodecahedral; Physical properties.

1. Introduction

In recent years, coordination complexes of lanthanides have drawn immense attention due to their versatile applications in various areas of chemical, biomedical and materials research. Lanthanide metal ions are very different when compared with transition metal ions. They have large ionic radii and hence they can easily form complexes with coordination numbers more than six and the accompanying uncommon coordination geometries.^{1,2} Trivalent lanthanides have very distinctive photophysical properties. They display large Stokes shifts and sharp emission bands from long-lived excited states. High magnetic moments, large magnetic anisotropy and the electron spin relaxation behaviors make the trivalent lanthanides unique with respect to their magnetic properties. All these features have led to the use of lanthanide complexes as chirality probes for biological substrates,^{3,4} photocytotoxic agents,⁵ luminescence sensors and imaging agents,^{6–8} photo-emitting materials,^{9–11} single molecule and single chain magnets^{12–15} and contrast agents in magnetic resonance imaging.^{16–19} Some lanthanide complexes are also used as catalysts in organic synthesis.^{20–22} Due to the above mentioned wide variety

of applications there is a continuous quest for new lanthanide complexes.

Recently, we have reported two mononuclear complexes of nickel(II) and copper(II) and a double helical dicopper(II) complex with the tetradentate Schiff base biacetyl bis(benzoylhydrazone) (H_2babh , 2 H's represent the two dissociable amide protons).^{23,24} In the mononuclear complexes, the dianionic ligand (babh^{2-}) provides the expected N_2O_2 square-plane around the metal centre and forms 5,5,5-membered fused chelate rings.²³ On the other hand, each bridging ligand in $[\text{Cu}_2(\mu\text{-babh})_2]$ is twisted along the single bond of its $=\text{C}(\text{CH}_3)\text{C}-\text{C}(\text{CH}_3)=$ fragment to accommodate the two metal centres.²⁴ Thus, apparently rigid babh^{2-} is rather flexible and can adopt an unusual bridging coordination mode to provide the double helical motif of the dicopper(II) complex. Since lanthanide ions can have high (> 6) coordination numbers and hence unusual coordination geometries, complexes of them with not so rigid tetradentate babh^{2-} is anticipated to be interesting. In this work, we have investigated the complexation behavior of H_2babh with cerium and gadolinium ions and isolated the octacoordinated dodecahedral cerium(IV) and gadolinium(III) complexes having the formulas $[\text{Ce}(\text{babh})_2]$ (**1**) and $[\text{Gd}(\text{babh})(\text{Hbabh})]$ (**2**), respectively (Chart 1). Herein we describe the syntheses, physical properties and crystal structures of these two complexes.

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Chart 1. H_2babh and its complexes with cerium(IV) and gadolinium(III).

2. Experimental

2.1 Materials

The Schiff base biacetyl bis(benzoylhydrazone) (H_2babh) was synthesized by following our previously reported procedure.²³ All other chemicals and solvents were of analytical grade available commercially and were used as received.

2.2 Physical measurements

A Thermo Finnigan Flash EA1112 series elemental analyzer was used for the microanalytical (CHN) measurements. Infrared spectra were recorded by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu UV-3600 UV-VIS-NIR spectrophotometer was used to record the electronic spectra. The 1H NMR spectrum of the cerium(IV) complex was collected on a Bruker 400 MHz NMR spectrometer. X-band EPR measurements with the gadolinium(III) complex were performed on a Jeol JES-FA200 spectrometer. A Digisun DI-909 conductivity meter was used to measure the solution electrical conductivities. Room temperature magnetic susceptibilities were measured using a Sherwood Scientific balance. Variable temperature magnetic susceptibility measurements were performed with the help of a Quantum Design SQUID VSM. Diamagnetic corrections calculated from Pascal's constants²⁵ were used to obtain the molar paramagnetic susceptibilities.

2.3 Synthesis of $[Ce(babh)_2]$ (**1**)

A methanol (4 mL) solution of KOH (40 mg, 0.71 mmol) was added to a methanol (25 mL) solution of H_2babh (100 mg, 0.31 mmol) and the mixture was stirred at 50°C for 1/2 h to obtain a clear solution. To this solution

a methanol (10 mL) solution of $CeCl_3 \cdot 6H_2O$ (53 mg, 0.15 mmol) was added slowly, refluxed for 1 h and then cooled to room temperature. The dark microcrystalline solid deposited was collected by filtration and dried in air. The yield was 80 mg (68%). Anal. calcd for $CeC_{36}H_{32}N_8O_4$: C, 55.38; H, 4.13; N, 14.35%. Found: C, 55.53; H, 4.21; N, 14.16%. UV-Vis in CH_2Cl_2 solution: λ (nm) (ϵ ($10^3 M^{-1} cm^{-1}$)) = 510sh (9.2), 400 (44.2), 365sh (40.3), 283 (61.9), 265sh (58.6).

2.4 Synthesis of $[Gd(babh)(Hbabh)] \cdot H_2O$ (**2**· H_2O)

A methanol (4 mL) solution of KOH (40 mg, 0.71 mmol) was added to a methanol (25 mL) solution of H_2babh (100 mg, 0.31 mmol) and stirred for 10 min at room temperature. Then a methanol (10 mL) solution of $Gd(NO_3)_3 \cdot 5H_2O$ (65 mg, 0.15 mmol) was added to the mixture of H_2babh and KOH and stirred for 7 hours. The resulting yellow solution was evaporated to about 5 mL. A yellow amorphous powder precipitated within 2-3 days was collected by filtration. The yield was 90 mg (73%). Anal. calcd for $GdC_{36}H_{35}N_8O_5$: C, 52.93; H, 4.32; N, 13.71%. Found: C, 52.95; H, 4.59; N, 13.48%. UV-Vis in CH_2Cl_2 solution: λ (nm) (ϵ ($10^3 M^{-1} cm^{-1}$)) = 460sh (27.1), 430sh (48.8), 415 (50.7), 305sh (30.4), 263 (43.2).

2.5 X-ray crystallography

Single crystals of the cerium(IV) complex (**1**) were obtained by diffusion of *n*-hexane into its dichloromethane solution as $1 \cdot CH_2Cl_2$. On the other hand, single crystals of the mono hydrated gadolinium(III) complex (**2**· H_2O) were grown by slow evaporation of its dichloromethane solution. A Bruker-Nonius SMART APEX CCD single crystal diffractometer equipped with a graphite monochromator and a Mo $K\alpha$ fine-focus

sealed tube ($\lambda = 0.71073 \text{ \AA}$) was used for the determination of unit cell parameters and intensity data collections at 100 K for each of **1**·CH₂Cl₂ and **2**·H₂O. The SMART software was used for data acquisition and the SAINT-Plus software was used for data extraction.²⁶ The absorption corrections were performed with the help of SADABS program.²⁷ The structures of **1**·CH₂Cl₂ and **2**·H₂O were solved in the monoclinic space groups *P*2₁/*c* and *C*2/*c*, respectively by direct methods and refined on *F*² by full-matrix least-squares procedures. In each case, the asymmetric unit contains a whole complex molecule with the corresponding solvent molecule. In case of **2**·H₂O, one of the phenyl rings of Hbabh[−] is disordered. Four carbon atoms of this phenyl ring are located at eight positions that are related by a two-fold axis passing through the remaining two *para* carbon atoms. The disordered carbon atoms located at eight positions (each having half site occupancy) were refined isotropically with geometric restraints. All non-hydrogen atoms in **1**·CH₂Cl₂ and those with full site occupancies in **2**·H₂O were refined using anisotropic thermal parameters. The hydrogen atoms of the water molecule in **2**·H₂O were located in a difference Fourier map and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$ and geometric restraints. The remaining hydrogen atoms in **2**·H₂O and all the hydrogen atoms in **1**·CH₂Cl₂ were included in the structure factor calculations at idealized positions by using a riding model. The SHELX-97 programs²⁸ available in the WinGX package²⁹ were used for structure solution and refinement. The Mercury³⁰ and Platon³¹

packages were used for molecular graphics. Selected crystallographic data are listed in table 1.

3. Results and Discussion

3.1 Synthesis

[Ce(babh)₂] (**1**) and mono hydrated [Gd(babh)(Hbabh)] (**2**·H₂O) have been synthesized in 68 and 73% yields, respectively by reacting one mole equivalent of the corresponding hydrated trivalent metal ion salt (CeCl₃·6H₂O and Gd(NO₃)₃·5H₂O), two mole equivalents of biacetyl bis(benzoylhydrazone) (H₂babh) and little more than four mole equivalents of KOH in methanol. **1** has been isolated as a dark microcrystalline material, while **2**·H₂O has been obtained as an amorphous yellow powder. The elemental (CHN) analysis data of **1** and **2**·H₂O are in good agreement with the corresponding molecular formulas. The room temperature (300 K) effective magnetic moment (μ_{eff}) value (8.03 μ_{B}) of **2**·H₂O is very close to the spin-only value expected for an f⁷ metal ion. Thus the gadolinium centre in **2** is in the trivalent state. On the other hand, the diamagnetic nature of **1** confirms the +4 oxidation state of its cerium centre. Both complexes are highly soluble in dichloromethane, chloroform, methanol, dimethylsulfoxide and acetone. **1** affords a brown solution whereas **2**·H₂O produces a yellow solution. Both complexes behave as non-electrolyte in solution.

Table 1. Selected crystallographic data for **1**·CH₂Cl₂ and **2**·H₂O.

Complex	1 ·CH ₂ Cl ₂	2 ·H ₂ O
Chemical formula	CeC ₃₇ H ₃₄ N ₈ O ₄ Cl ₂	GdC ₃₆ H ₃₅ N ₈ O ₅
Formula weight (g mol ^{−1})	865.74	816.98
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	11.5199(9)	27.003(6)
<i>b</i> (Å)	25.818(2)	20.395(5)
<i>c</i> (Å)	12.7913(11)	19.854(5)
β (°)	104.362(1)	128.806(3)
Volume (Å ³)	3685.6(5)	8521(3)
<i>Z</i>	4	8
Calculated density (g cm ^{−3})	1.560	1.274
Absorption coefficient (mm ^{−1})	1.431	1.601
Reflections collected	35070	29912
Unique reflections	6495	7474
Reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	6358	5228
Data/restraints/Parameters	6495/0/469	7474/40/455
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0231, 0.0581	0.0935, 0.2044
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0237, 0.0585	0.1354, 0.2212
Goodness-of-fit on <i>F</i> ²	1.124	1.140
Largest peak and hole (e Å ^{−3})	0.432, −0.497	2.693, −2.608

3.2 Molecular structures

The structures of **1**·CH₂Cl₂ and **2**·H₂O are illustrated in figure 1. The bond lengths and the bond angles related to the metal centres are given in table 2. In general, the metal to coordinating atom (O and N) bond lengths in **1** and **2** are within the ranges reported for cerium(IV) and gadolinium(III) complexes, respectively having similar coordinating atoms.^{32–34} In each of **1** and **2**, the ligands act as ONNO-donors and form 5,5,5-membered fused chelate rings and a distorted dodecahedral N₄O₄ coordination sphere around the metal centre (figure 2). The C–O (1.298(3)–1.304(2) Å) and the C–N bond lengths (1.308(3)–1.312(3) Å) of the –C(O[–])=N– fragments of the two ligands (babh^{2–}) are consistent with the deprotonated form of each of the four amide functionalities in **1**.^{23,24} On the other hand, the C(12)–O(2) (1.252(14) Å) and the C(12)–N(4) (1.379(14) Å) bond lengths are noticeably shorter and longer, respectively compared to the C–O (1.271(14)–1.299(14) Å) and the C–N bond lengths (1.291(14)–1.327(15) Å) of the other three amide functionalities in **2** (figure 1b). Thus, here one ligand (Hbabh[–]) has one protonated and one deprotonated amide functionality, while both amide functionalities of the other ligand (babh^{2–}) are deprotonated. In both **1** and **2**, 5,5,5-membered fused chelate rings formed by each ONNO-donor ligand excluding the phenyl rings are satisfactorily coplanar (mean deviations 0.03–0.11 Å). The dihedral angles between the two planes each containing 5,5,5-membered chelate

rings are 89.8(1)° and 83.1(1)° for **1** and **2**, respectively. Thus the two ligands are essentially orthogonal to each other and hence meridional in **1** as well as in **2** (figure 1). In both complexes, each phenyl ring is twisted along the C–C bond that connects it with the terminal chelate ring. In **1**, the dihedral angles formed by the two phenyl ring planes with the mean plane containing the corresponding 5,5,5-membered fused chelate rings span the range 9.5(1)°–18.9(1)°. In case of **2**, C(13)–C(18) phenyl ring is disordered (figure 1b). Four carbon atoms (C(14), C(15), C(17) and C(18)) of this phenyl ring are located at eight positions that are related by a two-fold axis passing through C(13) and C(16). The dihedral angles formed by these two orientations of the C(13)–C(18) phenyl ring with the plane containing the corresponding 5,5,5-membered fused chelate rings are 38(1)° and 56(1)°. The analogous dihedral angles for the remaining three phenyl rings are within 15(1)°–22.8(6)°.

3.3 Supramolecular structures

Supramolecular structures via intermolecular non-covalent interactions for both **1**·CH₂Cl₂ and **2**·H₂O have been scrutinized. The solvent molecules trapped in the crystal lattices play crucial roles in directing the supramolecular structures by participating in intermolecular hydrogen bonding interactions. These hydrogen bonds are unconventional for **1**·CH₂Cl₂, while they are conventional for **2**·H₂O (table 3). In addition to the

Figure 1. Structures of (a) [Ce(babh)₂]·CH₂Cl₂ (**1**·CH₂Cl₂) and (b) [Gd(babh)(Hbabh)]·H₂O (**2**·H₂O). All non-hydrogen atoms are represented by 50% (in **1**·CH₂Cl₂) and 30% (in **2**·H₂O) probability thermal ellipsoids. For clarity, a few carbon atoms are not labeled and only one orientation of the disordered phenyl ring (C13–C18) of **2**·H₂O is shown.

hydrogen bonds, π - π interactions also take part in shaping the final supramolecular structure of $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$.

In the crystal lattice, $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ units exist as dimers. In the dimeric unit, each CH_2Cl_2 participate in a

Table 2. Selected bond lengths (Å) and angles (°) for $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ and $\mathbf{2} \cdot \text{H}_2\text{O}$.

Bond parameter	$\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ (M = Ce)	$\mathbf{2} \cdot \text{H}_2\text{O}$ (M = Gd)
M–O(1)	2.2671(15)	2.326(8)
M–O(2)	2.2651(15)	2.408(9)
M–O(3)	2.2650(15)	2.326(7)
M–O(4)	2.2719(15)	2.313(8)
M–N(2)	2.5095(18)	2.503(10)
M–N(3)	2.5073(18)	2.564(9)
M–N(6)	2.5101(17)	2.494(9)
M–N(7)	2.5089(18)	2.489(9)
O(1)–M–O(2)	171.37(5)	171.8(3)
O(1)–M–O(3)	88.94(6)	95.8(3)
O(1)–M–O(4)	91.10(6)	90.0(3)
O(1)–M–N(2)	63.22(6)	63.8(3)
O(1)–M–N(3)	125.33(5)	124.8(3)
O(1)–M–N(6)	90.71(5)	94.5(3)
O(1)–M–N(7)	89.55(5)	88.9(3)
O(2)–M–O(3)	91.82(6)	86.4(3)
O(2)–M–O(4)	89.40(5)	89.3(3)
O(2)–M–N(2)	125.40(6)	124.2(3)
O(2)–M–N(3)	63.30(6)	63.3(3)
O(2)–M–N(6)	81.97(5)	79.3(3)
O(2)–M–N(7)	82.97(6)	83.5(3)
O(3)–M–O(4)	171.69(5)	167.9(3)
O(3)–M–N(2)	83.06(5)	87.8(3)
O(3)–M–N(3)	85.35(5)	82.3(3)
O(3)–M–N(6)	63.28(5)	64.7(3)
O(3)–M–N(7)	125.03(5)	126.7(3)
O(4)–M–N(2)	89.54(6)	85.2(3)
O(4)–M–N(3)	87.86(6)	85.6(3)
O(4)–M–N(6)	125.03(5)	125.5(3)
O(4)–M–N(7)	63.28(5)	63.9(3)
N(2)–M–N(3)	62.11(6)	61.0(3)
N(2)–M–N(6)	138.23(6)	143.8(3)
N(2)–M–N(7)	141.82(6)	139.2(3)
N(3)–M–N(6)	132.49(6)	131.5(3)
N(3)–M–N(7)	136.13(6)	135.3(3)
N(6)–M–N(7)	61.80(5)	61.9(3)

$\text{C–H} \cdots \text{N}$ interaction involving the babh^{2-} amidate-N atom of one complex molecule and a $\text{C–H} \cdots \text{Cl}$ interaction involving the babh^{2-} phenyl *ortho* C–H of a second complex molecule (table 3). Thus, two CH_2Cl_2 molecules bridge two $[\text{Ce}(\text{babh})_2]$ molecules via two $\text{C–H} \cdots \text{N}$ and two $\text{C–H} \cdots \text{Cl}$ hydrogen bonds and form the centrosymmetric $\{\mathbf{1} \cdot \text{CH}_2\text{Cl}_2\}_2$ unit (figure 3). The phenyl rings (C(6)–C(11) and C(13)–C(18)) of one babh^{2-} ligand in the $[\text{Ce}(\text{babh})_2]$ molecules of each $\{\mathbf{1} \cdot \text{CH}_2\text{Cl}_2\}_2$ unit are involved in π - π interactions (~ 3.7 Å centroid-to-centroid distance) with the two adjacent dimeric units. As a result, a one-dimensional π -stacked assembly of $\{\mathbf{1} \cdot \text{CH}_2\text{Cl}_2\}_2$ is formed (figure 3). These intermolecular $\text{C–H} \cdots \text{N}$, $\text{C–H} \cdots \text{Cl}$ and π - π interactions assisted self-assembly pattern of $\mathbf{1} \cdot \text{CH}_2\text{Cl}_2$ can be best described as ‘ladder’ type where, the steps are formed by the hydrogen bonds and the two sides are made by the π - π interactions (figure 3).

In $\mathbf{2} \cdot \text{H}_2\text{O}$, the water molecule is involved in three intermolecular hydrogen bonds (table 3). It acts as acceptor in a strong $\text{N–H} \cdots \text{O}$ hydrogen bond involving the protonated amide functionality of Hbabh^- and donor in two $\text{O–H} \cdots \text{N}$ hydrogen bonds involving the amidate-N atoms of two babh^{2-} ligands of two adjacent complex molecules. Thus each water molecule is connected to three complex molecules. Self-assembly via these intermolecular $\text{N–H} \cdots \text{O}$ and $\text{O–H} \cdots \text{N}$ hydrogen bonds leads to a two-dimensional ‘sheet’ like network of $\mathbf{2} \cdot \text{H}_2\text{O}$ (figure 4).

3.4 Spectroscopic characteristics

The amide functionality N–H and C=O stretches are observed as a medium intensity band at $\sim 3200 \text{ cm}^{-1}$ and a strong band at $\sim 1655 \text{ cm}^{-1}$, respectively in the infrared spectrum of the free Schiff base H_2babh .^{23,35} In case of $\mathbf{1}$, absence of both these bands confirms the deprotonated state of the amide functionalities of both coordinated ligands. In contrast, $\mathbf{2} \cdot \text{H}_2\text{O}$ exhibits a

Figure 2. Dodecahedral coordination spheres around the metal centres in $\mathbf{1}$ and $\mathbf{2}$.

Table 3. Hydrogen-bond parameters for **1**·CH₂Cl₂ and **2**·H₂O.

Complex	D–H···A	d(D···A) (Å)	<(DHA) (°)
1 ·CH ₂ Cl ₂	C(37)–H(37B)···N(4)	3.348(3)	143
	C(29)–H(29)···Cl(2) ^a	3.566(2)	138
2 ·H ₂ O	N(4)–H(4)···O(5)	2.821(12)	168
	O(5)–H(5A)···N(5) ^b	2.924(12)	173
	O(5)–H(5B)···N(8) ^c	2.889(13)	160

Symmetry transformations used to generate equivalent atoms:

^a–x, –y, –z ^bx, –y, z + 1/2 ^c–x + 1/2, y – 1/2, –z + 1/2. **Figure 3.** The ladder type structure formed by [Ce(babh)₂]·CH₂Cl₂ (**1**·CH₂Cl₂) via C–H···N, C–H···Cl and π – π interactions.

medium intensity band at 1624 cm^{–1}. This band is most likely associated with the metal coordinated C=O stretch of the protonated amide functionality in Hbabh[–]. However, no band assignable to the N–H group of the protonated amide functionality could be detected presumably due to its participation in the N–H···O hydrogen bonding with the water molecule (*vide supra*). Instead, the broad relatively weak band observed at ~3400 cm^{–1} is perhaps associated with the hydrogen bonded water molecule. Both complexes display the C=N stretch as a medium intensity band at ~1590 cm^{–1}.

The electronic spectra of **1** and **2**·H₂O have been collected using the corresponding dichloromethane solutions. The spectra are shown in figure 5. The cerium(IV) complex (**1**) displays a prominent shoulder at ~510 nm and two strong and broad bands at 400 nm and 283 nm each followed by a shoulder. The gadolinium(III) complex (**2**·H₂O) shows two similar strong and broad absorptions at 415 nm and 263 nm with several shoulders. Overall the spectral profiles of the two complexes are quite similar except for the 510 nm shoulder in the spectrum of **1**. In general, f–f transitions are sharp and

unaffected by ligand field effect.³⁶ In dichloromethane, H₂babh displays a single strong absorption at 305 nm. Thus, for both complexes the absorption observed below 300 nm is attributed to intraligand transitions, while the absorption in the visible region is assigned to ligand-to-metal charge transfer transitions.^{23,24,37,38}

The ¹H NMR spectrum of the cerium(IV) complex (**1**) has been recorded using its CDCl₃ solution. The protons of the four methyl groups of the two babh^{2–} ligands resonate as a singlet at δ 2.77 ppm. The *ortho* and the *para* protons of the four phenyl groups (two from each ligand) resonate as doublets at δ 7.95 ppm (J = 7.2 Hz) and δ 7.35 ppm (J = 7.2 Hz), respectively. The *meta* protons are observed as a triplet at δ 7.30 ppm (J = 7.2 Hz).

The EPR spectra of the seven-electron paramagnetic gadolinium(III) complex (**2**·H₂O) in powder phase at room temperature (298 K) and in frozen (150 K) dichloromethane are depicted in figure 6. Both spectra display several signals over the broad range of 0–750 mT. The profiles of the two spectra are quite similar except for the 0–300 mT region. In this region, the powder spectrum shows two broad signals, while each

Figure 4. Two-dimensional network of $[\text{Gd}(\text{babh})(\text{Hbabh})] \cdot \text{H}_2\text{O} (2 \cdot \text{H}_2\text{O})$ through $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds.

Figure 5. Electronic spectra of $[\text{Ce}(\text{babh})_2]$ (1) (—) and $[\text{Gd}(\text{babh})(\text{Hbabh})] \cdot \text{H}_2\text{O} (2 \cdot \text{H}_2\text{O})$ (---) in dichloromethane.

of these two broad signals splits into three or more signals in the frozen solution spectrum. Above 300 mT both spectra display several relatively weak signals. Such EPR spectral profiles with multiple signals over a

Figure 6. EPR spectra of $[\text{Gd}(\text{babh})(\text{Hbabh})] \cdot \text{H}_2\text{O} (2 \cdot \text{H}_2\text{O})$ in powder phase at 300 K (top) and in frozen (150 K) dichloromethane (bottom).

broad field range are quite common for gadolinium(III) complexes with $S = 7/2$ spin state due to the zero-field and Zeeman effects.^{37,39,40}

Figure 7. Temperature dependent effective magnetic moment (μ_{eff}) (Δ) and inverse molar magnetic susceptibility (χ_{M}^{-1}) (O) of $[\text{Gd}(\text{babh})(\text{Hbabh})]\cdot\text{H}_2\text{O}$ ($2\cdot\text{H}_2\text{O}$). The solid line represents the best least-squares fit using the parameters given in the text.

3.5 Cryomagnetic properties of $2\cdot\text{H}_2\text{O}$

Variable temperature magnetic susceptibility measurements with a powdered sample of the gadolinium(III) complex ($2\cdot\text{H}_2\text{O}$) have been performed in the temperature range 300–3 K. The μ_{eff} values at 300 and 40 K are 8.03 and 7.98 μ_{B} , respectively. Thus there is essentially no change of the μ_{eff} in the temperature range 300–40 K (figure 7). Between 40–10 K there is a gradual small decrease of the μ_{eff} and it reaches the value of 7.85 μ_{B} at 10 K. Below 10 K it decreases rather sharply by a relatively larger amount and reaches the value of 6.93 μ_{B} at 3 K. Crystal structure shows a hydrogen bond assisted two-dimensional ‘sheet’ like network of $2\cdot\text{H}_2\text{O}$ (*vide supra*). Thus, the decrease of the μ_{eff} by about 1.1 μ_{B} in the temperature range 40–3 K is perhaps due to weak intermolecular antiferromagnetic interactions between the metal centres. Nonetheless, least-squares fit of the data over the entire temperature range (300–3 K) to the Curie-Weiss law, $\chi_{\text{M}} = C/(T - \theta)$ indicates essentially Curie paramagnetic behaviour of $2\cdot\text{H}_2\text{O}$ (figure 7). The best fit provided the Weiss constant θ as -0.7 K and Curie constant C as 8.1 emu K mol $^{-1}$.

4. Conclusions

Complexes of cerium(IV) and gadolinium(III) with biacetyl bis(benzoylhydrazone) (H_2babh) have been synthesized. They are characterized as $[\text{Ce}(\text{babh})_2]$ (**1**) and $[\text{Gd}(\text{babh})(\text{Hbabh})]\cdot\text{H}_2\text{O}$ ($2\cdot\text{H}_2\text{O}$) with the help of elemental analysis, X-ray crystallographic, spectroscopic and magnetic susceptibility measurements.

The physical properties of both complexes are consistent with the corresponding metal ion oxidation states and molecular formulas. X-ray structures of the solvated complexes, **1** $\cdot\text{CH}_2\text{Cl}_2$ and $2\cdot\text{H}_2\text{O}$, reveal 5,5,5-membered fused chelate rings forming ONNO-coordinating mode of babh^{2-} and Hbabh^- . Two such meridionally disposed ligands form a distorted dodecahedral N_4O_4 coordination sphere around the metal centre in each of **1** and **2**. Both **1** $\cdot\text{CH}_2\text{Cl}_2$ and $2\cdot\text{H}_2\text{O}$ are involved in intermolecular non-covalent interactions in their corresponding crystal lattices. These are $\text{C}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{N}$ and $\pi-\pi$ interactions for **1** $\cdot\text{CH}_2\text{Cl}_2$, and $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds for $2\cdot\text{H}_2\text{O}$. Supramolecular self-assembly via these interactions leads to a one-dimensional ‘ladder’ type structure and a two-dimensional ‘sheet’ like network for **1** $\cdot\text{CH}_2\text{Cl}_2$ and $2\cdot\text{H}_2\text{O}$, respectively.

Supplementary Information

CCDC-1012274 and CCDC-1012275 contain the supplementary crystallographic data for **1** $\cdot\text{CH}_2\text{Cl}_2$ and $2\cdot\text{H}_2\text{O}$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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