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Mononuclear Al^{III}, Ga^{III} and In^{III}, and heterodinuclear $Ga^{III}M^{II}$ (M = Zn, Cu, Ni, Co) complexes of a tetraiminodiphenol macrocyclic ligand†

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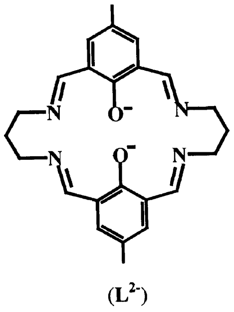
Received (in Montpellier, France) 27th May 2005, Accepted 29th June 2005
First published as an Advance Article on the web 20th July 2005

Mononuclear aluminium(III), gallium(III) and indium(III) complexes $[M^{III}(LH_2)(H_2O)Cl](ClO_4)_2\cdot nH_2O$ (**1–3**) of the tetraiminodiphenolate macrocyclic ligand L^{2-} have been synthesized. The two uncoordinated imine nitrogens of these compounds are protonated and hydrogen bonded to the metal-bound phenolate oxygens to stabilize them against hydrolytic cleavage. The gallium(III) compound, **2**, forms the heterodinuclear complexes $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)(H_2O)][ClO_4]$ (M = Co, **4**; Ni, **5**) and $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)][ClO_4]\cdot 2H_2O$ (M = Cu, **6**; Zn, **7**). The presence of the core unit $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)]^+$ in all the compounds has been ascertained by ESI-MS measurements. Complexes **1–3** show luminescence at room temperature between 505 and 490 nm. Spectrofluorimetric titrations of **2** with $Zn(OAc)_2\cdot 2H_2O$ and $Cu(OAc)_2\cdot H_2O$ in acetonitrile have shown that the formation of a 1 : 1 $Ga^{III}Zn^{II}$ complex occurs with the growth of luminescence intensity, while the formation of a $Ga^{III}Cu^{II}$ complex leads to the complete quenching of luminescence. Complexes **1–7** have been further characterized by their proton NMR spectra.

Introduction

There is considerable current interest in the chemistry of Group-13 metal elements because of their involvement in the genesis and diagnosis of diseases. Aluminium(III) has been suspected[1] of inducing neurological dysfunctions such as Alzheimer's disease, even though overwhelming medical evidence still does not convincingly demonstrate even a causal relationship between aluminium and the disease.[2] On the other hand, complexes of gallium(III) and indium(III) have strong potential as radiopharmaceuticals.[3–5] The radioisotopes ^{67}Ga (γ, $t_{\frac{1}{2}}$ = 3.25 d), ^{68}Ga (β^+, $t_{\frac{1}{2}}$ = 68 min) and ^{111}In (γ, $t_{\frac{1}{2}}$ = 2.80 d) have appropriate energies and half-lives for γ-ray imaging and positron emission tomography. For effective transportation of these radioisotopes to the target organs, the thermodynamic stability of the complex species should be high, and could be achieved by using polydentate ligands. To this end, extensive studies have been made in recent years on the chemistry of Group-13 metals with various polydentate ligands comprising combinations of amino and phenolic units.[6–9] Interestingly, however, similar complexes of iminophenol ligands are not reported. This is probably because the Lewis acidity of the trivalent Group-13 metal ions induces hydrolytic cleavage of the CH=N bonds in these ligands. Nevertheless, a recent study has reported[10] the structures of several gallium(III), indium(III) and thalium(III) complexes of a hexadentate tripodal iminophenol ligand by synthesizing these complexes in an improved way.

Although numerous studies have been reported on the phenoxo-bridged homodimetallic complexes of tetraiminodiphenolate macrocyclic ligands,[11–17] non-availability of metal-free macrocyclic ligands has restricted these studies to divalent metal ions. We have reported[18] valence delocalization phenomenon in the mixed-valence $Fe^{II}Fe^{III}$ tetraiminodiphenol macrocyclic systems. More recently, we reported[19] the efficient proton-templated synthesis of a whole range of tetraiminodiphenol macrocyclic ligands as their perchlorate salts. These macrocyclic ligands and their dizinc(II) complexes exhibit strong luminescence.[17,19] The present study is concerned with the synthesis and spectroscopic characterization of the mononuclear complexes $[M^{III}(LH_2)(H_2O)Cl](ClO_4)_2\cdot nH_2O$ (M = Al, Ga, In) and the heterodinuclear complexes $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)][ClO_4]\cdot nH_2O$ (M = Co, Ni, Cu, Zn) derived from the macrocyclic ligand (L^{2-}), **I**.



I

Experimental

Materials

Reagent grade chemicals obtained from commercial sources were used as received. Solvents were purified and dried according to standard methods.[20] The chloride salts of aluminium, gallium and indium were prepared by treating the metal with dilute HCl, followed by evaporation of the solution over a steam bath. The residue was dissolved in water, filtered, concentrated to a viscous liquid and kept in a desiccator over

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† Electronic supplementary information (ESI) available: Simulated and observed ESI-MS positive spectral patterns of **4**, **5** and **7**, absorption spectra of **4–6** and ^1H NMR spectrum of **5**. See http://dx.doi.org/10.1039/b507484c

DOI: 10.1039/b507484c

dried silica gel. 2,6-diformyl-4-methylphenol was prepared according to a literature method.[21] $[Pb(LH_2)][ClO_4]_2$ was prepared as reported earlier.[22]

Preparation of the complexes

Caution! All the perchlorate salts reported in this study are potentially explosive and therefore should be handled with care.

Mononuclear complexes $[M(LH_2)(H_2O)Cl](ClO_4)_2 \cdot nH_2O$ [M = Al, Ga, In] (1–3). To a boiling acetonitrile solution (50 cm^3) of $[Pb(LH_2)](ClO_4)_2$ (0.81 g, 1 mmol) were added simultaneously acetonitrile solutions (20 cm^3) of the metal chloride (1 mmol) and sodium perchlorate (0.55 g, 4 mmol). The resulting yellow solution was refluxed for 1 h, after which time the precipitated $PbCl_2$ was removed by filtration. The filtrate was concentrated at 80 °C to a volume of *ca.* 40 cm^3, at which point an orange or yellow crystalline product began to separate out. At this stage, the solution was kept overnight for slow evaporation. The deposited crystalline compound was filtered and washed with acetonitrile and diethyl ether.

$[Al(LH_2)(H_2O)Cl](ClO_4)_2$ (1). Yield 0.36 g (53%). Found C, 42.56; H, 4.46; N, 7.98. $C_{24}H_{30}N_4O_{11}AlCl_3$ requires C, 42.14; H, 4.39; N, 8.19%. IR data on KBr (ν/cm^{-1}) 3406br, 2932m, 2866w, 1646s, 1532s, 1460w, 1387w, 1337m, 1308w, 1210m, 1129s, 1088s, 996m, 883w, 678w, 629m and 572w. δ_H (300 MHz, CD_3CN) 13.40 (2 H, s, N–H···O), 8.26 (4 H, s, CH=N), 7.26 (4 H, s, Ar), 3.97 (8 H, s, α-CH_2), 2.25 (4 H, s, β-CH_2) and 2.11 (6 H, s, CH_3).

$[Ga(LH_2)(H_2O)Cl](ClO_4)_2$ (2). Yield 0.39 g (54%). Found C, 39.33; H, 4.12; N, 8.12. $C_{24}H_{30}N_4O_{11}GaCl_3$ requires C, 39.65; H, 4.13; N, 7.71%. IR data on KBr (ν/cm^{-1}) 3408br, 2927m, 2866w, 1650s, 1556s, 1448m, 1352m, 1288m, 1236m, 1113s, 1088s, 870w, 830w, 685w, 629m and 525w. δ_H (300 MHz, $(CD_3)_2SO$) 11.86 (2 H, s, N–H···O), 8.64 (2 H, s, CH=N in the metal free site), 8.55 (2 H, s, CH=N in the metal site), 7.59 (2 H, s, Ar in the metal free site), 7.55 (2 H, s, Ar in the metal site), 3.99 (4 H, s, α-CH_2 in the metal free site), 3.89 (4 H, s, α-CH_2 in the metal site), 2.28 (6 H, s, CH_3), 2.15 (2 H, s, β-CH_2 in the metal free site) and 2.07 (2 H, s, β-CH_2 in the metal site).

$[In(LH_2)(H_2O)Cl](ClO_4)_2 \cdot 2H_2O$ (3). Yield 0.45 g (56%). Found C, 35.61; H, 4.17; N, 6.81. $C_{24}H_{34}N_4O_{13}InCl_3$ requires C, 35.66; H, 4.21; N, 6.93%. IR data on KBr (ν/cm^{-1}) 3410br, 2945m, 2859w, 1656s, 1551s, 1454m, 1348m, 1295w, 1248m, 1121s, 1086s, 923w, 877w, 811w, 685w, 628m and 519w. δ_H (300 MHz, CD_3CN) 12.37 (2 H, s, N–H···O), 8.48 (2 H, s, CH=N in the metal free site), 8.27 (2 H, s, CH=N in the metal site), 7.62 (2 H, s, Ar in the metal free site), 7.54 (2 H, s, Ar in the metal site), 4.37 (2 H, s, α-CH_2 in the metal free site), 3.85 (2 H, s, α-CH_2 in the metal free site), 4.20 (2 H, s, α-CH_2 in the metal site), 4.12 (2 H, s, α-CH_2 in the metal site), 2.28 (6 H, s, CH_3) and 2.24 (2 H, s, β-CH_2).

Heterodinuclear $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)][ClO_4] \cdot nH_2O$ complexes [M = Co, Ni, Cu and Zn] (4–7). To a stirred acetonitrile solution (50 cm^3) of **2** (0.36 g, 0.5 mmol) at room temperature were added an acetonitrile solution (10 cm^3) of $M(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) and solid sodium acetate (0.16 g, 2 mmol). The colour of the solution changed from yellow to pink (for Co^{II}), greenish-yellow (for Ni^{II}) or green (for Cu^{II}). After stirring for 3 h, the solution was filtered and the filtrate concentrated on a rotary evaporator to dryness. The residue was extracted with dichloromethane (30 cm^3) and the extract concentrated to a volume of *ca.* 10 cm^3. The solution was then kept at *ca.* 5 °C for a few hours. The crystalline product that deposited was collected by filtration and washed with diethyl ether. The compounds rapidly lose crystallinity upon standing in air.

$[Ga^{III}Co^{II}L(\mu\text{-}OAc)(OAc)(H_2O)][ClO_4]$ (4). Brown compound, yield 0.22 g (57%). Found C, 43.91; H, 4.40; N, 7.28. $C_{28}H_{34}N_4O_{11}GaCoCl$ requires C, 43.86; H, 4.44; N, 7.31%. MS (ESI positive in CH_3CN) m/z = 691 $[Ga^{III}Co^{II}L(OAc)(ClO_4)]^+$, 649 $[Ga^{III}Co^{II}L(OAc)_2]^+$ and 295.5 $[Ga^{III}Co^{II}L(OAc)]^{2+}$. IR data on KBr ($\nu$/$cm^{-1}$) 3410br, 2925m, 2866w, 1644s, 1595sh, 1570s, 1443m, 1408m, 1322m, 1275w, 1117s, 1084s, 943w, 883w, 808w, 678w, 628m and 539w. δ_H (300 MHz, CD_3CN) 144, 120, 96, 43.6, 19.9, 10.7, 6.9, 2.36, 2.04 and −6.2.

$[Ga^{III}Ni^{II}L(\mu\text{-}OAc)(OAc)(H_2O)][ClO_4]$ (5). Light yellow compound, yield 0.20 g (52%). Found C, 43.76; H, 4.46; N, 7.30. $C_{28}H_{34}N_4O_{11}GaNiCl$ requires C, 43.87; H, 4.44; N, 7.31%. MS (ESI positive in CH_3CN) m/z = 690 $[Ga^{III}Ni^{II}L(OAc)(ClO_4)]^+$, 650 $[Ga^{III}Ni^{II}L(OAc)_2]^+$ and 296 $[Ga^{III}Ni^{II}L(OAc)]^{2+}$. IR data on KBr ($\nu$/$cm^{-1}$) 3408br, 2925m, 2866w, 1650s, 1595w, 1572s, 1443m, 1407m, 1320m, 1274w, 1245w, 1209w, 1122s, 1083s, 937w, 883w, 808m, 771w, 628m and 525w. δ_H (300 MHz, $(CD_3)_2SO$) 178, 120, 63, 24.2, 11.3, 9.3, 6.03, 4.72 and −5.59.

$[Ga^{III}Cu^{II}L(\mu\text{-}OAc)(OAc)][ClO_4] \cdot 2H_2O$ (6). Green compound, yield 0.23 g (59%). Found C, 42.45; H, 4.52; N, 7.09; $C_{28}H_{36}N_4O_{12}GaCuCl$ requires C, 42.60; H, 4.56; N, 7.10%. MS (ESI positive in CH_3CN) m/z = 695 $[Ga^{III}Cu^{II}L(OAc)(ClO_4)]^+$, 655 $[Ga^{III}Cu^{II}L(OAc)_2]^+$ and 298.5 $[Ga^{III}Cu^{II}L(OAc)]^{2+}$. IR data on KBr ($\nu$/$cm^{-1}$) 3409br, 2925m, 2860w, 1642s, 1576s, 1444m, 1415m, 1385m, 1322s, 1277w, 1243w, 1113s, 1086s, 931w, 878w, 816m, 763w, 667w, 627m and 523w. δ_H (300 MHz, CD_3CN) 22, 13.4, 11.2, 9.1, 4.9, 3.6, 3.05 and −9.6.

$[Ga^{III}Zn^{II}L(\mu\text{-}OAc)(OAc)][ClO_4] \cdot 2H_2O$ (7). Yellow compound, yield 0.25 g (64%). Found C, 42.49; H, 4.50; N, 7.10; $C_{28}H_{36}N_4O_{12}GaZnCl$ requires C, 42.50; H, 4.55; N, 7.08%. MS (ESI positive in CH_3CN) m/z = 696 $[Ga^{III}Zn^{II}L(OAc)(ClO_4)]^+$, 656 $[Ga^{III}Zn^{II}L(OAc)_2]^+$and 299 $[Ga^{III}Zn^{II}L(OAc)]^{2+}$. IR data on KBr ($\nu$/$cm^{-1}$) 3432br, 2932m, 2859w, 1640s, 1590sh, 1567s, 1438m, 1416m, 1374m, 1334m, 1279w, 1243m, 1198w, 1088s, 1003w, 937w, 897w, 822m, 769, 623m and 519w. δ_H (300 MHz, CD_3CN) 8.28 (2 H, s, CH=N Ga site), 8.24 (2 H, s, CH=N Zn site), 7.39 (4 H, s, Ar), 4.07 (4 H, s, α-CH_2 Ga site), 3.98 (4 H, s, α-CH_2 Zn site), 2.30 (6 H, s, CH_3), 2.18 (2 H, s, β-CH_2 Ga site), 2.08 (2 H, s, β-CH_2 Zn site) and 1.54 (6 H, s, CH_3 of OAc).

Physical measurements

Elemental C, H and N analyses were performed on a Perkin-Elmer 2400II elemental analyzer. The ^1H NMR (300 MHz) spectra were performed in CD_3CN (**1**, **3**, **4**, **6** and **7**) and $(CD_3)_2SO$ solutions (**2** and **5**) on a Bruker Avance DPX-300 spectrometer. Longitudinal relaxation times, T_1, were measured by the inversion recovery method. FTIR spectra were recorded using KBr disks on a FT-IR Nexus Nicolet spectrometer. The electronic spectra of **1–7** in acetonitrile were measured in the range 250–1100 nm using Shimadzu UV-2100 and 1601PC spectrophotometers. Emission spectral measurements were carried on a Perkin-Elmer LS55 luminescence spectrometer with 10^{-5} mol dm^{-3} acetonitrile solutions. Emission quantum yields, φ, were measured at room temperature in acetonitrile solution relative to perylene as the standard.[23] The quantum yields were calculated using the relation[24]

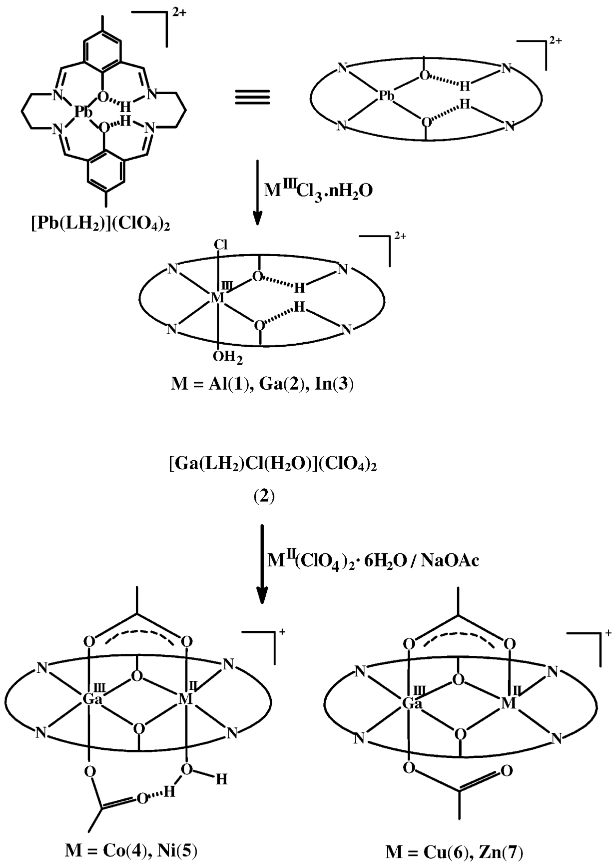
$$\varphi = \varphi_{\mathrm{std}}\ (A_{\mathrm{std}}/A)(I/I_{\mathrm{std}})(\eta^2/\eta^2_{\mathrm{std}})$$

where A, I, and η refer to absorbance, integrated emission intensity, and solution refractive index, respectively. The electrospray ionization mass spectra (ESI-MS positive) of compounds **4–7** were measured in acetonitrile on a Micromass Qtof YA263 mass spectrometer.

Results and discussion

Synthesis

The cyclocondensation reaction between 2,6-diformyl-4-methylphenol and 1,3-diaminopropane in the presence of the chloride salts of aluminium(III), gallium(III) or indium(III) fail to produce the corresponding dinuclear or mononuclear macrocyclic complexes $[M_2^{III}L]^{4+}$ and $[M^{III}L]^{+}$. The lack of formation of the dinuclear complexes can be attributed to Coulombic charge repulsion between the metal centres, while the failure to produce $[M^{III}L]^{+}$ species seems to be due to the susceptibility of the uncoordinated CH=N bonds in such compounds to hydrolytic cleavage. We have reported[19] that the nucleophilic attack on uncoordinated CH=N bonds can be prevented by protonating the imino nitrogens under mild conditions. Thus, when one equivalent of lead(II) perchlorate is reacted with two equivalents each of 2,6-diformyl-4-methylphenol, 1,3-diaminopropane and acetic acid, the mononuclear complex $[Pb(LH_2)][ClO_4]_2$ is obtained in high yield.[21] In this compound, the two protonated imine nitrogens are hydrogen bonded with the lead(II)-bound phenolate oxygens and the compound in solution is stable towards hydrolysis. As shown in Scheme 1, the metathetical reaction between the hydrated chloride salts of aluminium(III), gallium(III) or indium(III) and $[Pb(LH_2)][ClO_4]_2$ produces the corresponding $[M^{III}(LH_2)(H_2O)Cl](ClO_4)_2 \cdot nH_2O$ complex, **1–3**. The gallium(III) complex, **2**, on reaction with the hydrated perchlorate salts of cobalt(II), nickel(II), copper(II) or zinc(II) in a 1 : 1 ratio, in the presence of excess of sodium acetate, produces the acetate-bridged heterodinuclear complexes $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)][ClO_4] \cdot nH_2O$, **4–7**. All the heterodinuclear complexes were initially isolated in a crystalline form, however, attempts to determine their crystal structures were unsuccessful as their crystallinity was lost within a few minutes of being taken out of the mother liquor. The composition of the compounds reported here are based on analyses of products which were first stored for *ca.* 24 h. Complexes **1–7** were found to be stable toward hydrolytic decomposition. Although they were insoluble in water, they could be recovered unchanged from a 1 : 1 acetonitrile–water solution.



Scheme 1

Mass spectra

The electrospray ionization mass spectra (ESI-MS positive) of the heterodinuclear complexes **4–7** have been measured using their acetonitrile solutions (*ca.* 10^{-4} mol dm^{-3}). All the compounds exhibit similar spectral features, and are characterized by the occurrence of three types of positively-charged species. Namely, these are $[Ga^{III}M^{II}L(OAc)(ClO_4)]^{+}$, $[Ga^{III}M^{II}L(OAc)_2]^{+}$ and $[Ga^{III}M^{II}L(OAc)]^{2+}$, with the relative abundance of the doubly-positive charged ion being the highest. Fig. 1 shows the cluster of peaks observed for the three types of molecular cations of **6**, along with their corresponding simulated spectral patterns. It may be noted that the numbers of peaks, m/z values and the relative peak heights observed for the cations $[Ga^{III}Cu^{II}L(OAc)(ClO_4)]^{+}$, $[Ga^{III}Cu^{II}L(OAc)_2]^{+}$ and $[Ga^{III}Cu^{II}L(OAc)]^{2+}$ are in excellent agreement with the calculated spectral patterns obtained by taking into consideration the relative abundances of the isotopes of the constituent elements. Similar observations are made for complexes **4**, **5** and **7** (Figs. S1–S3).† From the mass spectral studies, it is clear that all the heterodinuclear complexes contain the core cation $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)]^{+}$.

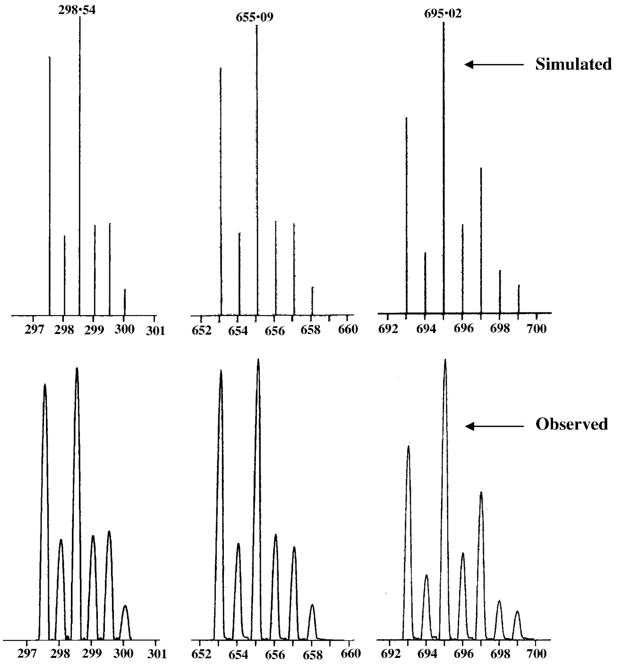


Fig. 1 Electrospray ionization mass spectra (ESI-MS positive) of $[Ga^{III}Cu^{II}L(\mu\text{-}OAc)(OAc)][ClO_4]$, **6**, in acetonitrile. Simulated isotropic spectral patterns are compared with the observed major positively-charged cationic species.

Infrared spectra

The common IR spectral features observed for complexes **1–7** are a broad band due to water in the range 3500–3400 cm^{-1}, a strong band due to $\nu_{C{=}N}$ between 1655 and 1640 cm^{-1} and characteristic bands due to ionic perchlorate at *ca.* 1100 and 630 cm^{-1}. The heterodinuclear complexes **4–7** exhibit additional bands due to their coordinated acetates. Thus, the ν_{asym} CO_2^- vibrations are observed as a shoulder and as a strong band at about 1595 and 1570 cm^{-1} respectively, whereas the ν_{sym} CO_2^- vibrations are observed as two medium intensity bands at about 1440 and 1410 cm^{-1}. The differences in energies, Δ, of the ν_{asym} and ν_{sym} vibrations ($1595 - 1410 = 185$ cm^{-1} and $1570 - 1440 = 130$ cm^{-1}) indicate the presence of two types of acetate group. Generally for bidentate carboxylates, the Δ value is less than 100 cm^{-1}, for unidentate acetate Δ is greater than 150 cm^{-1}, while for bridging carboxylate the Δ value is close to 150 cm^{-1}.[25] On the basis of this classification, the presence of both bridging and unidentate acetate in **4–7** may be anticipated.

Absorption spectra

The absorption spectral data of complexes **1–7** in acetonitrile are listed in Table 1. The mononuclear complexes **1–3** exhibit two strong absorptions at 250–260 and 390–430 nm. Significantly for the aluminium compound, the lower energy absorption band occurs at a considerably higher wavelength (430 nm) compared to that of gallium (390 nm) and indium (395 nm).

In the heterodinuclear $Ga^{III}M^{II}$ compounds **4–7**, the positions of the two absorption bands in the UV region remain practically unchanged for all the four compounds, and are observed at about 255 and 365 nm. For the $Ga^{III}Co^{II}$ compound, **4**, a weak broad absorption occurs at *ca.* 950 nm ($\varepsilon = 8$ dm^3 mol^{-1} cm^{-1}). This band seems to be due to the $^4T_1(F) \rightarrow {}^4T_{2g}$ transition of the six-coordinated cobalt(II) centre. The $Ga^{III}Ni^{II}$ compound, **5**, on the other hand, exhibits three absorption bands in the visible region with λ_{max} at 560 nm ($\varepsilon = 17$ dm^3 mol^{-1} cm^{-1}), 830 nm ($\varepsilon = 3$ dm^3 mol^{-1} cm^{-1}) and 1070 nm ($\varepsilon = 3$ dm^3 mol^{-1} cm^{-1}). These absorptions can be related to $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), $^3T_{1g}$ and $^3T_{2g}$ transitions for octahedral nickel(II), in decreasing order of energy. In the $Ga^{III}Cu^{II}$ complex, **6**, the sole d–d band, typical of square pyramidal copper(II), is observed at 645 nm ($\varepsilon = 45$ dm^3 mol^{-1} cm^{-1}). As expected, the $Ga^{III}Zn^{II}$ compound, **7**, shows no absorption in the visible region. The absorption spectra of **4–6** are available as supplementary information (Figs. S4–S6).†

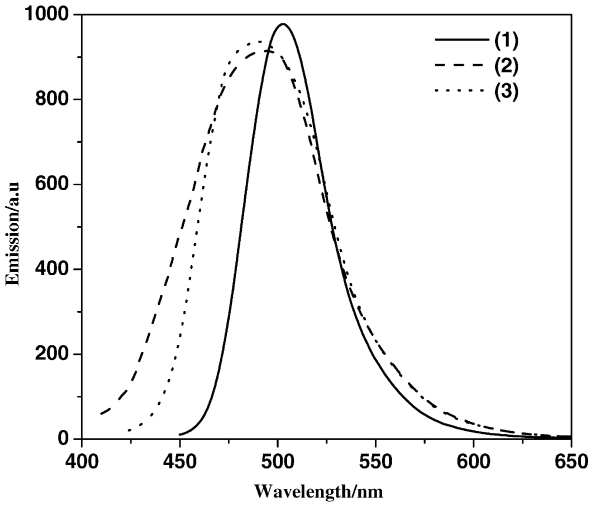


Fig. 2 Luminescence spectra observed for the mononuclear complexes **1–3** in acetonitrile at room temperature.

Luminescence spectra

The mononuclear compounds show luminescence at room temperature when their acetonitrile solutions are irradiated with light in the wavelength range 390–430 nm. For compound **1**, the intensity of luminescence becomes maximum, with a peak at 505 nm, when the excitation wavelength is 430 nm. On the other hand for **2**, λ_{em} occurs at 495 nm with $\lambda_{ex} = 390$ nm; while for **3**, the emission occurs at 490 nm when it is excited at 395 nm. The emission spectral characteristics of these compounds are given in Table 1. It may be noted that the Stoke's shift decreases in the following way: **2** (5450 cm^{-1}) > **3** (4900 cm^{-1}) > **1** (3500 cm^{-1}). As shown in Fig. 2, at the appropriate excitation wavelengths, the emission intensities of all the three compounds are essentially the same. All the three compounds lose luminescence when their solutions are treated with triethylamine.

Spectrofluorimetric titrations carried out by adding an incremental amount of an acetonitrile solution of $Zn(OAc)_2 \cdot 2H_2O$ to a solution of **2** in the same solvent, leading to the formation of **7**, is shown in Fig. 3. The growth of the emission band at 435 nm, using 390 nm as the excitation wavelength, was monitored. The inset of Fig. 3 shows that with the increase in mole fraction of $Zn(OAc)_2 \cdot 2H_2O$ added, the luminescence intensity increases smoothly and then tapers off in the vicinity of a 1 : 1 ratio of gallium(III) and zinc(II). With the further addition of zinc(II), no further change in luminescence intensity occurs.

Table 1 Absorption and emission spectral data for complexes **1–7**[a]

Compounds	Absorption λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission λ_{max}/nm	Emission φ
1	250 (26 500), 430 (15 700)	505	0.07
2	260 (30 200), 390 (12 400)	495	0.09
3	260 (24 600), 395 (9 800)	490	0.10
4	255 (49 600), 368 (9 200), 945 (8)	—	—
5	255 (57 300), 370 (11 100), 560 (17), 830 (3), 1070 (3)	—	—
6	255 (59 200), 368 (10 800), 650 (45)	—	—
7	255 (46 600), 370 (9 500)	435	—

[a] In acetonitrile.

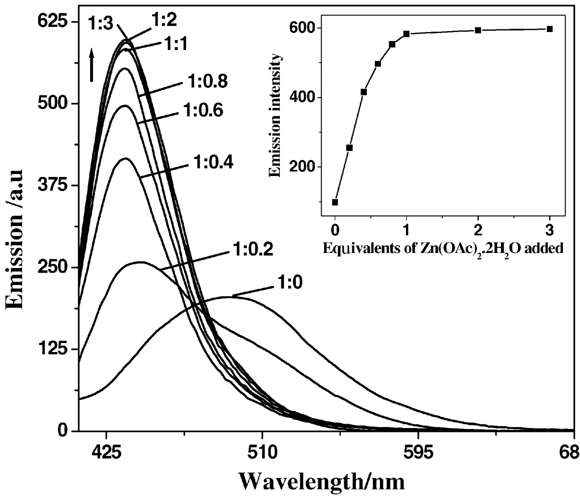


Fig. 3 Spectrofluorimetric titration of $[Ga(LH_2)(H_2O)Cl][ClO_4]_2$ (1×10^{-5} mol dm^{-3}) with increasing equivalents of $Zn(OAc)_2 \cdot 2H_2O$ in acetonitrile. The excitation wavelength used was 390 nm. The inset shows the variation of luminescence intensity with the number of equivalents of $Zn(OAc)_2 \cdot 2H_2O$ added.

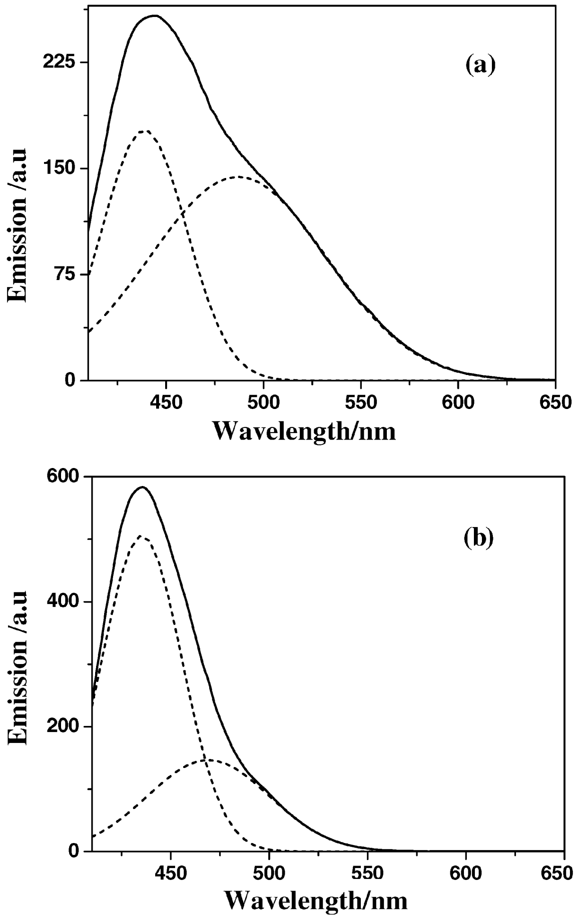


Fig. 4 Deconvoluted luminescence spectra for the mixture of $[Ga(LH_2)(H_2O)Cl][ClO_4]_2$ and $Zn(OAc)_2 \cdot 2H_2O$ in acetonitrile in the ratio (a) 1 : 0.2 and (b) 1 : 1.

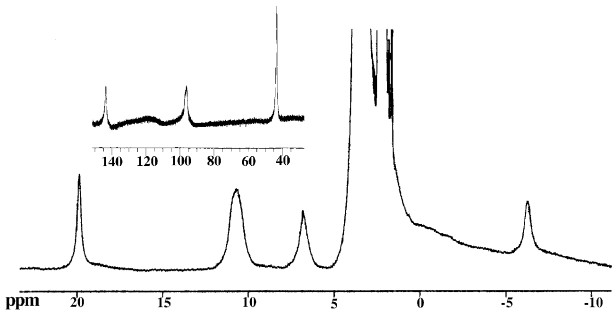


Fig. 6 ^1H NMR spectrum of $[Ga^{III}Co^{II}L(\mu\text{-}OAc)(OAc)(H_2O)][ClO_4]$, **4**, in CD_3CN.

On careful examination, the luminescence spectra obtained during the titration (Fig. 3) reveals the occurrence of dual luminescence. This is illustrated in Fig. 4, where the spectra observed for the solutions containing **2** and $Zn(OAc)_2 \cdot 2H_2O$ in the ratios 1 : 0.2 (Fig. 4(a)) and 1 : 1(Fig. 4(b)) are deconvoluted. Fig. 4(a) shows the presence of two peaks at 435 and 490 nm, while Fig. 4(b) shows that although the position of the first peak remains unchanged, the second peak is blue-shifted to 470 nm. Indeed, for all the emission spectra obtained during titration, deconvolution shows that the emission peak observed at 490 nm for the solution containing gallium(III) alone is gradually shifted to 470 nm when gallium (III) to zinc(II) ratio becomes 1 : 1, without showing any significant change of luminescence intensity. On the other hand, as the gallium(III) to zinc(II) ratio changes from 1 : 0 to 1 : 1, the intensity of luminescence also increases, albeit the peak position remains unchanged at 435 nm. Clearly, in the heterodinuclear $Ga^{III}Zn^{II}$ compound, the dual emission occurs due to the non-equivalence of the structural sites. Fig. 4(b) shows that relative to the gallium(III) site, the zinc(II) site is more photoluminescent. We have recently reported [17] that the dizinc(II) complex $[Zn_2L(\mu\text{-}OAc)][ClO_4] \cdot 2H_2O$ shows strong luminescence in acetonitrile, with λ_{em} at 430 nm when λ_{ex} is 370 nm. Importantly, the observed normalized intensity of the dizinc(II) complex is almost double that of the zinc(II) site in **7**.

In contrast to the $Ga^{III}Zn^{II}$ complex, **7**, the other $Ga^{III}M^{II}$ complexes, **4–6**, are devoid of photoluminescence. The quenching of the luminescence of **2** occurs when it is treated with a transition metal(II) salt, and this is typically shown in Fig. 5—where an acetonitrile solution of **2** is titrated with $Cu(OAc)_2 \cdot H_2O$. The inset of Fig. 5 shows that the total loss of luminescence occurs with the formation of the $Ga^{III}Cu^{II}$ complex, **6**.

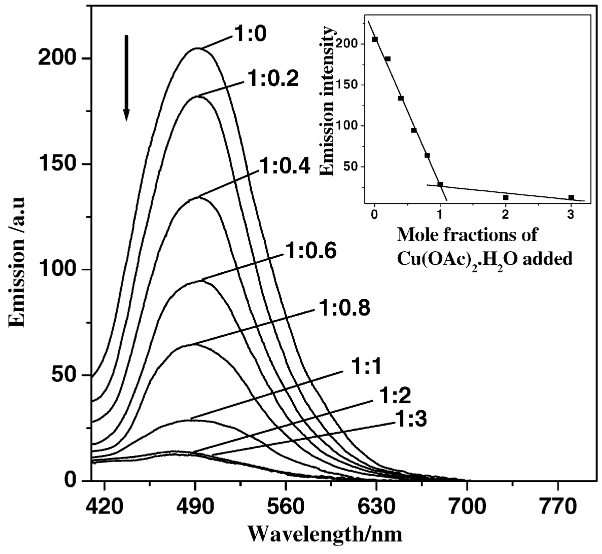


Fig. 5 Quenching of luminescence intensity during the titration of $[Ga(LH_2)(H_2O)Cl][ClO_4]_2$ (1×10^{-5} mol dm^{-3}) with $Cu(OAc)_2 \cdot H_2O$ in acetonitrile. The excitation wavelength used was 390 nm. The inset shows the variation in emission intensity with the mole fraction of $Cu(OAc)_2 \cdot H_2O$ added.

Proton NMR spectra

The ^1H NMR spectra of **1**, **3**, **4**, **6** and **7** were measured in CD_3CN, while for **2** and **5** their $(CD_3)_2SO$ solutions were used. For the diamagnetic compounds **1–3** and **7**, the observed chemical shifts and assignments are given in the Experimental section. In the mononuclear compounds **1–3**, the protonated imine nitrogens, which are intramolecularly hydrogen bonded with the phenolate oxygens, are observed as broad singlets at 13.40, 11.86 and 12.37 ppm respectively. As expected, the $Ga^{III}Zn^{II}$ compound, **7**, shows small differences in the chem-

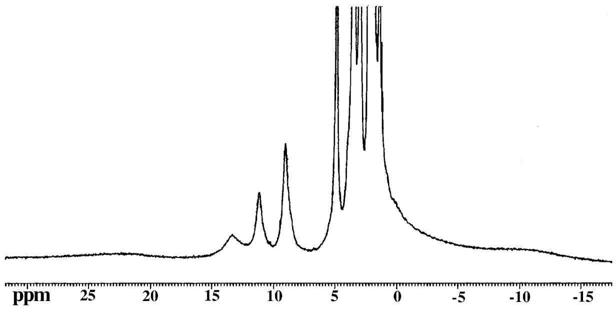
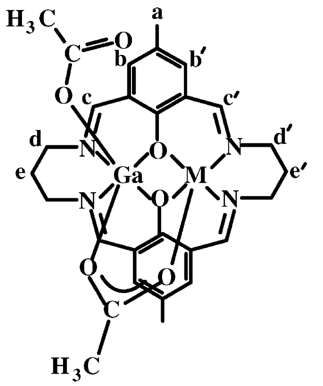


Fig. 7 ^1H NMR spectrum of $[Ga^{III}Cu^{II}L(\mu\text{-}OAc)(OAc)][ClO_4] \cdot 2H_2O$, **6**, in CD_3CN.

Table 2 Chemical shifts, T_1 values, line widths and assignments for $Ga^{III}M^{II}$ compounds **4–6**

$Ga^{III}Co^{II}$, **4**				$Ga^{III}Ni^{II}$, **5**			$Ga^{III}Cu^{II}$, **6**			
δ/ppm	T_1/ms	$\Delta_{\frac{1}{2}}$/Hz[a]	Assignment	δ/ppm	$\Delta_{\frac{1}{2}}$/Hz[a]	Assignment	δ/ppm	T_1/ms	$\Delta_{\frac{1}{2}}$/Hz[a]	Assignment
144	—	220	d′	178	1400	d′	—	—	—	—
120	—	1080	μ-OAc	120	850	μ-OAc	22	—	1300	μ-OAc
96	3.4	180	b′	63	1200	b′	13.4	—	350	b′
43.6	8.2	120	c	24.2	112	c	11.2	4.5	190	c
19.9	12.4	86	b	11.3	170	b	9.1	17.2	175	b
10.7	18.9	154	d	9.3	142	d	4.9	12.7	70	d
6.9	15.8	132	e	6.03	135	e	3.6	32.4	50	a
2.36	27.6	15	a	4.72	27	a	3.05	16.5	80	e
2.04	22.4	18	OAc	—	—	—	—	—	—	—
−6.2	10.9	130	e′	−5.59	620	e′	−9.6	—	2240	e′

[a] Full width at half height.



Scheme 2

ical shifts for the identical protons in proximity to the gallium(III) and zinc(II) centres.

In the paramagnetic compounds, hyperfine-shifted resonances are observed due to interactions between nuclear spins and unpaired electron spins, in addition to the normal diamagnetic nuclear spin interactions. Electron and nuclear spin interactions occurring through bonds give rise to a contact shift, while through space interactions give rise to a dipolar or pseudo-contact shift. The dipolar shift depends on the magnetic anisotropy of the system and the position in space of a given proton. The contribution of the contact shift decreases rapidly with the increase in the number of bonds connecting the proton to the paramagnetic centre. However, when the unpaired electron spin is delocalized, the interaction remains significant for protons many bonds away from the metal centre. For the assignment of signals in paramagnetic compounds, measurement of longitudinal relaxation times, T_1, and transverse relaxation times, T_2, are particularly important. T_1 correlates the proximity of the proton to paramagnetic centre, while $T_2 = 1/\pi(fwh)$, where *fwh* is full width of a signal at its half-height, correlates line width to the proximity of the proton to the paramagnetic site. The closer the proximity of a proton to the metal centre, the shorter the T_1 and the broader the line width.[26]

Fig. 6 and Fig. 7 show the ^1H NMR spectra of $Ga^{III}Co^{II}$, **4**, and $Ga^{III}Cu^{II}$, **6**, compounds respectively, while the spectrum of $Ga^{III}Ni^{II}$, **5**, is available as supplementary information (Fig. S7).† The assignment of signals (the numbering scheme for the protons is shown in Scheme 2) based on T_1 values, line widths and intensities are given in Table 2. It may be noted that of the three compounds, the widths of the signals observed for the Ga $^{III}Co^{II}$ compound are relatively lower, which is consistent with the behaviour expected for high-spin Co^{II}, for which electronic relaxation time is short.

Conclusion

The tendency of CH=N bonds to be hydrolyzed in the presence of Group-13 metal (III) ions is the major deterrent for the synthesis of Schiff base complexes of these metals. Nevertheless, complexes of the type $[M^{III}(LH_2)(H_2O)Cl][ClO_4]_2$ have been obtained for aluminium(III), gallium(III) and indium (III) with a tetraiminodiphenolate macrocyclic ligand, L^{2-}. In these compounds, the two uncoordinated imine nitrogens, which are protonated and involved in intramolecular hydrogen bonding with the phenolate oxygens, contribute to the reinforcement of the stability of the compounds. Spectrofluorimetric titrations of $[Ga^{III}(LH_2)(H_2O)Cl]^{2+}$ with the acetate salts of zinc(II) and copper(II) have shown that the formation of 1 : 1 complex species is accompanied by the maximization of luminescence intensities for zinc and the complete quenching of luminescence for copper. The heterodinuclear complexes $[Ga^{III}M^{II}L(\mu\text{-}OAc)(OAc)]^+$ have been isolated as their perchlorate salts for cobalt(II), nickel(II), copper(II) and zinc(II). The hyperfine-shifted ^1H NMR spectral features of the paramagnetic compounds have been analyzed using their longitudinal relaxation times, T_1, and line widths.

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