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2,2′-Bipyridine,1,10-phenanthroline and 2,2′:6′,2″-terpyridine in gallium(III) chemistry: Complexes containing the $\{Ga^{III}_2(\mu\text{-}OH)_2\}^{4+}$ core

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Abstract

The reactions of $Ga(NO_3)_3 \cdot 9H_2O$ with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy) in alcohols afford the complexes $[Ga_2(OH)_2(bpy)_4](NO_3)_4$ (**1**), $[Ga_2(OH)_2(phen)_4](NO_3)_4$ (**2**) and $[Ga_2(OH)_2(H_2O)_2(terpy)_2](NO_3)_4$ (**3**), respectively, in good yields. The crystal structures of $\mathbf{1} \cdot 1.3MeOH \cdot 1.4H_2O$, $\mathbf{2} \cdot 4.5MeOH$ and **3** have been solved by single-crystal X-ray crystallography. The three complexes contain the $\{Ga^{III}_2(\mu\text{-}OH)_2\}^{4+}$ core. Four nitrogen atoms from two chelating bpy (**1**) or phen (**2**) complete distorted octahedral coordination at each metal centre. In **3** one tridentate chelating terpy and one aquo ligand complete six coordination at each Ga^{III} atom. The crystal structure of $\mathbf{2} \cdot 4.5MeOH$ is stabilized by hydrogen bonds and intermolecular π–π stacking interactions, while in **3** hydrogen bonds create a double-chain, ladder-like architecture. Characteristic IR data are discussed in terms of the nature of bonding and the structures of the three complexes. The ^1H NMR spectra of complexes **2** and **3** suggest the presence of the free ligand and one solution species containing the coordinated ligand. The structure of the cation $[Ca_2(OH)_2(bpy)_4]^{4+}$ is retained in D_2O as deduced by the 2D homonuclear COSY map.

Keywords: 2,2′-Bipyridine gallium(III) complexes; Bis(hydroxo)gallium(III) complexes; COSY NMR spectra; 1,10-Phenanthroline gallium(III) complexes; 2,2′:6′,2″-Terpyridine gallium(III) complexes

1. Introduction

The last two decades have witnessed a remarkable growth in the interest in the coordination chemistry of gallium(III). This has been mainly due to its relevance to three fields: materials science, medicinal chemistry, and bioinorganic chemistry. In the first field, binary compounds of Ga(III) with the Group 15 elements, often prepared by relatively low-temperature decomposition of simple complexes [1], have emerged as leading materials for optoelectronic devices such as light-emitting diodes and laser diodes in the blue/UV region [2,3]. In recent years, the most promising candidates to replace $[Alq_3]$ as electron-transport host or emitting material [4] for organic light-emitting diodes (OLEDs) [5] are thought to be complexes with Ga^{III} as the central atom [6]. Also a great deal of attention has been paid to the synthesis of open-framework phosphate-based gallium(III) materials [7], especially since the discovery of crystalline aluminophosphate molecular sieves in 1982 [8]. The interest arises from the ability of Ga^{III} to exist in a more variable and expanded coordination environment, as opposed to zeolites and aluminophosphates that contain

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only tetrahedrally coordinated units. For example, Yang and co-workers recently reported [9] the first example of a layered inorganic–organic hybrid gallium(III) phosphate with a neutral framework, a type of material that may find application in intercalation reactions.

In the medicinal chemistry arena, the interest arises from the incorporation of gallium(III) radionuclides ($^{67}Ga^{3+}$, $^{68}Ga^{3+}$) into diagnostic radiopharmaceuticals [10], the antitumour activity of $GaCl_3$, $Ga(NO_3)_3$ and few gallium(III) complexes [11], and the *in vitro* anti-HIV (HIV = human immunodeficiency virus) activity of $Ga(NO_3)_3$ and some $GaCl_3$/L complexes (L = various azoles) [12]. Thus, gallium-labelled radiopharmaceuticals have been used for either γ scintigraphy or PET imaging in a broad range of clinical pathologies. Introduced in 1969 as a tumour imaging agent [13], ^{67}Ga-citrate still remains a clinically useful radiopharmaceutical [14]; it has been shown to detect a large variety of tumours as well as inflammation/infection sites and skeletal disorders [15,16]. The antineoplastic properties of gallium(III) were recognised almost 30 years ago. The safety and activity of simple gallium(III) salts, mainly intravenous $Ga(NO_3)_3$, have been extensively studied in clinical trials since 1975 [17]. Whereas this salt is an effective drug for the treatment of hypercalcemia of malignancy and has been approved for this medication, its unfavorable pharmacokinetic properties have prevented its widespread use in chemotherapy of cancer patients [18]. Parenteral administration as bolus infusion is associated with a low therapeutic index due to renal toxicity, while oral administration is inefficient due to non-effective intestinal absorption. Development of tumour-inhibiting gallium(III) complexes has been pursued as a strategy to circumvent the limitations faced with simple salts [12,18]. For example, complex $[GaL_2][GaCl_4]$ (L = 2-acetylpyridine ^4N-dimethylthiosemicarbazonate) exhibits excellent antiproliferative activity, as demonstrated by *in vitro* experiments in human cell lines derived from different types of solid tumours [18].

A third interesting point in the coordination chemistry of gallium(III) is as the diamagnetic biological mimic of iron(III) [2]. For instance, diamagnetic Ga(III) analogues of the microbial Fe(III) chelates (siderophores) have been useful in NMR studies [19], since the native Fe(III) species are paramagnetic. The basis for the replacement of Fe^{3+} by Ga^{3+} lies in the similar radii of the two metal ions. In reverse, the knowledge gained from studies of Fe^{3+} transport has been applied to the development of $^{67}Ga^{3+}$ radiopharmaceuticals [20].

Our interest in the coordination chemistry of Ga(III) [21–25] is focused on the medicinal [21,25] and bioinorganic chemistry [23] of this metal ion. Concerning the medicinal chemistry viewpoint, we have embarked on a programme aiming at the synthesis, characterization, and evaluation of the antitumour and antiviral activities of gallium(III) chloride [21,25] and sulfate [24] complexes of *N*-heterocycles. Since $Ga(NO_3)_3$ is involved in the treatment of hypercalcemia of malignancy, we have decided to extend our efforts investigating the reactions of this salt with *N*-heterocycles. The *chemical* aspects of our investigation are reported in this paper, whereas the *biological* activity of the resultant complexes will be described in a future report.

The initially chosen ligands for our studies are 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy). These ligands have played an important role in the development of coordination chemistry. However, their complexes with Ga(III) are limited in number. In this context, we describe herein the synthetic exploration of the general $Ga(NO_3)_3 \cdot 9H_2O$/L reaction system, where L is bpy, phen or terpy. The products from these reaction systems are all dinuclear complexes that contain the $\{Ga_2^{III}(\mu-OH)_2\}^{4+}$ core. The study of oxo/hydroxo-bridged Ga(III) complexes is attracting increasing attention because information about oligomerization and polymerization permits control of the structure, composition, and morphology of solid particles in the preparation of new materials [26,27]. It should be stressed at this point that while this paper was at the stage of writing, Junk and co-workers [28] reported the X-ray structures of complexes $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 5H_2O$ and $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 4H_2O$. The molecular structures of the cations of these complexes are similar to the molecular structure of $[Ga_2(OH)_2(bpy)_4]^{4+}$ which is present in our complex $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 1.3MeOH \cdot 1.4H_2O$ (**1** $\cdot$ 1.3MeOH $\cdot$ 1.4 H_2O) described here. However, the tetra-hydrate compound is crystallized in a different crystal system (triclinic versus monoclinic in our complex), while the structure of the penta-hydrate compound (prepared in $MeNO_2$) was solved in a different monoclinic space group ($P2_1/c$ versus $C2/c$) than that used in our complex (prepared in MeOH). Since the penta- and tetra-hydrates are different from **1** $\cdot$ 1.3 MeOH $\cdot$ 1.4H_2O in strict crystallographic viewpoint and since the later was characterized by IR and NMR spectroscopic techniques (such studies are lacking for the penta- and tetra-hydrates), we have decided to incorporate **1** $\cdot$ 1.3 MeOH $\cdot$ 1.4H_2O in this paper.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using reagent grade materials (Alfa Aesar, Aldrich) and solvents as received. Microanalyses (C, H, N) were performed by the University of Ioannina (Ioannina, Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. The metal content was determined gravimetrically with a 5% solution of 8-hydroxyquinoline in 2 M CH_3COOH; the pH was adjusted, pH 7, using 5 M aqueous NH_3. IR spectra (4000–450 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. 1D and 2D NMR spectra were recorded at 300 K on a Bruker Avance 400-MHz

spectrometer operating at 400.13 MHz. 1D spectra were acquired with and without presaturation of the H_2O signal and a recycle delay of 1–1.5 s using spectral width of 12–16 ppm DQF-COSY [29a] and TOCSY [29b,29c] experiments were performed in order to facilitate the identification of scalar connectivities between neighboring protons. TOCSY experiments were carried out by using the MLEV-17 spin-lock sequence and a mixing time of 80–100 ms. All 2D spectra consisted of 2K data points in the F2 dimension, and 16–32 transients and 1024 complex increments in the F1 dimension. All 2D maps were acquired with a spectral width of 12 ppm. Raw data were multiplied in both dimensions by a pure cosine-squared bell window function and Fourier-transformed to obtain 2048×1024 or 2048×2048 real data points. A polynomial base-line correction was applied in both directions. NMR data processing was performed using the standard Bruker software package on a Silicon Graphics O2 workstation. The 2D maps were analyzed on Silicon Graphics O2 or on PentiumIII PC-Linux computers with the aid of the program XEASY (ETH, Zürich) [29d].

2.2. Compound preparation

2.2.1. $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 1.3MeOH \cdot 1.4H_2O$ (**1** $\cdot 1.3MeOH \cdot 1.4H_2O$)

To a colourless solution of bpy (0.119 g, 0.76 mmol) in MeOH (10 ml) was slowly added a solution of $Ga(NO_3)_3 \cdot 9H_2O$ (0.100 g, 0.24 mmol). The resulting pale yellow solution was kept under stirring for about 5 min, and then was allowed to slowly concentrate at room-temperature. After 3 days, colourless X-ray quality prisms formed; they were collected by filtration, washed with cold MeOH (2×3 ml) and Et_2O (3×3 ml), and dried in air. Yield: 65% (based on the metal). The dried sample analysed as **1** $\cdot H_2O$. *Anal*. Calc. for $C_{40}H_{36}Ga_2N_{12}O_{15}$: C, 45.14; H, 3.42; N, 15.80; Ga, 13.10. Found: C, 45.49; H, 3.28; N, 16.06; Ga, 12.80%. IR (KBr, cm^{-1}): 3452s, 3310sh, 3118m, 3032w, 1762w, 1644m, 1614m, 1606s, 1576m, 1502m, 1480m, 1448s, 1384sb, 1322m, 1250w, 1160m, 1108w, 1066w, 1048w, 1030s, 826m, 768s, 730s, 662m, 652w, 642w, 506m, 492w.

2.2.2. $[Ga_2(OH)_2(phen)_4](NO_3)_4 \cdot 4.5MeOH$ (**2** $\cdot 4.5MeOH$)

Using phen $\cdot H_2O$ (0.172 g, 0.87 mmol) and $Ga(NO_3)_3 \cdot 9H_2O$ (0.121 g, 0.29 mmol) and following exactly the same procedure as that described for the corresponding bpy complex, colourless crystals of the product were isolated; the total volume of MeOH was 30 ml. Yield: 75% (based on the metal). The dried sample analysed as solvent-free. *Anal.* Calc. for $C_{48}H_{34}Ga_2N_{12}O_{14}$: C, 50.46; H, 3.01; N, 14.72; Ga, 12.21. Found: C, 49.95; H, 3.14; N, 14.97; Ga, 13.00%. IR (KBr, cm^{-1}): 3418mb, 3040w, 1762w, 1632m, 1614m, 1586w, 1524m, 1494w, 1432s, 1384s, 1260sh, 1228m, 1144m, 1110m, 1026mb, 874m, 852s, 826m, 738m, 720s, 654m, 518m, 494m.

2.2.3. $[Ga_2(OH)_2(H_2O)_2(terpy)_2](NO_3)_4$(**3**)

An aqueous solution (20 ml) of $Ga(NO_3)_3 \cdot 9H_2O$ (0.088 g, 0.21 mmol) was slowly added to a pale yellow solution of terpy (0.072 g, 0.31 mmol) in MeOH (20 ml) under vigorous stirring. The resulting colourless solution was evaporated to dryness under vacuum at 45–50 °C and the white solid redissolved in EtOH (20 ml). The new homogeneous, almost colourless solution was allowed to stand in a closed flask at room-temperature for 4 days; during this time X-ray quality colourless crystals of the product were precipitated. The crystals were collected by filtration, washed with ice-cold EtOH (1 ml) and Et_2O (2×1 ml), and dried in vacuo over silica gel. Yield: 50% (based on the metal). IR (KBr, cm^{-1}): 3508mb, 3444mb, 2924w, 1608m, 1578w, 1482m, 1458m, 1430sh, 1384s, 1354s, 1228m, 1162m, 1094w, 1028w, 778m, 734w, 656m.

2.3. Single-crystal X-ray crystallography

Crystals of **1** $\cdot 1.3MeOH \cdot 1.4H_2O$ and **2** $\cdot 4.5MeOH$ were mounted in capillary, whereas a crystal of **3** was mounted in air and covered with epoxy glou. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer with graphite-monochromated Mo radiation (**1** $\cdot 1.3MeOH \cdot 1.4H_2O$ and **3**) and an a $P2_1$ Nicolet diffractometer upgraded by Crysta l Logic using graphite-monochromated Cu radiation (**2** $\cdot 4.5MeOH$). Complete crystal data and parameters for data collection and processing are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the ranges $11 < 2\theta < 23°$ for **1** $\cdot 1.3MeOH \cdot 1.4H_2O$ and **3** and $22 < 2\theta < 54°$ for **2** $\cdot 4.5MeOH$. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and Ψ-scan absorption corrections were applied using Crystal Logic software. For **1** $\cdot 1.3MeOH \cdot 1.4H_2O$, the reflections collected in the 2θ range 45–50° were more than 60% unobserved and thus they have not been used in the refinement of the structure.

The structures were solved by direct methods using SHELXS-86 [30] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [31]. For **1** $\cdot 1.3MeOH \cdot 1.4H_2O$ and **2** $\cdot 4.5MeOH$, all hydrogen atoms were introduced at calculated positions as riding on bonded atoms; for the latter, the hydrogen atoms of the hydroxo groups were located by difference maps and those of the solvate molecules were not included in the refinement. For **3**, all hydrogen atoms were located by difference maps and were refined isotropically. For **2** $\cdot 4.5H_2O$ and **3**, all non-hydrogen atoms were refined using anisotropic thermal parameters. For **1** $\cdot 1.3MeOH \cdot 1.4MeOH$, all non-hydrogen atoms were refined anisotropically, except those of the solvate molecules which were refined isotropically with fixed occupation factors.

Table 1
Crystallographic data for complexes **1** · 1.3MeOH · 1.4H_2O, **2** · 4.5MeOH and **3**

Parameter	**1** · 1.3MeOH · 1.4H_2O	**2** · 4.5MeOH	**3**
Formula	$C_{41.3}H_{42}Ga_2N_{12}O_{16.7}$	$C_{52.5}H_{52}Ga_2N_{12}O_{18.5}$	$C_{30}H_{28}Ga_2N_{10}O_{16}$
Formula weight	1113.11	1286.50	924.06
Crystal colour, habit	Colourless, prism	Colourless, cube	Colourless, prism
Crystal dimensions (mm)	0.10 × 0.20 × 0.40	0.15 × 0.15 × 0.40	0.20 × 0.45 × 0.52
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	14.363(7)	11.278(2)	10.344(4)
b (Å)	25.166(13)	14.471(2)	10.724(3)
c (Å)	13.617(7)	20.019(3)	8.616(3)
α (°)	90	110.82(1)	82.60(1)
β (°)	106.72(2)	91.98(1)	89.45(1)
γ (°)	90	107.96(1)	69.51(1)
V(Å^3)	4714(4)	2866.6(7)	887.2(5)
Z	4	2	1
$\rho_{calc.}$ (g cm^{-3})	1.568	1.490	1.730
Radiation, λ (Å)	Mo Kα, 0.71073	Cu Kα, 1.54180	Mo Kα, 0.71073
Temperature (K)	298	298	298
Scan mode/speed (° min^{-1})	$\theta - 2\theta$/1.0	$\theta - 2\theta$/3.0	$\theta - 2\theta$/4.0
$2\theta_{max}$(°)	50	113	50
μ (mm^{-1})	1.229	1.872	1.609
Reflections collected/unique (R_{int})	3218/3065 (0.0228)	7993/7559 (0.0201)	3367/3137 (0.0089)
Data with $I > 2\sigma$(I)	2092	5868	2980
Parameters refined	327	813	319
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.668, −0.355	0.689, −0.525	0.976, −0.545
Goodness-of-fit (on F^2)	1.059	1.044	1.064
R_1[a], wR_2[b] (all data)	0.1043, 0.1775	0.0686, 0.1584	0.0335, 0.0824
R_1[a], wR_2[b] $I > 2\sigma >$ (I)	0.0628, 0.1555	0.0498, 0.1387	0.0314, 0.0807

[a] $R_1 = \sum(|F_o|-|F_c|)/\sum(|F_o|)$.

[b] $wR_2 = \left\{\sum\left[w\left(F_o^2 - F_c^2\right)^2\right] \Big/ \sum\left[w\left(F_o^2\right)^2\right]\right\}^{1/2}$.

3. Results and discussion

3.1. Brief synthetic comments

The formation of the Ga(III) complexes can be summarized in balanced equations (1) and (2), where L is bpy or phen.

$$2Ga(NO_3)_3 \cdot 9H_2O + 4L \xrightarrow{MeOH} \underset{\mathbf{1},\ \mathbf{2}}{[Ga_2(OH)_2L_4](NO_3)_4} + 2HNO_3 + 16H_2O \quad (1)$$

$$2Ga(NO_3)_3 \cdot 9H_2O + 2terpy \xrightarrow{MeOH-EtOH} \underset{\mathbf{3}}{[Ga_2(OH)_2(H_2O)_2(terpy)_2](NO_3)_4} + 2HNO_3 + 14H_2O. \quad (2)$$

The three complexes presumably form as a result of partial hydrolysis arising from the presence of water in the starting materials and the solvents. Five features of the reactions represented by Eqs. (1) and (2) deserve comments. First, the exact chemical identity of the products depends on the *N*-heterocycle present. The *bidentate* chelating ligands bpy and phen give dinuclear complexes with an 1:2 Ga^{III}: ligand ratio, whereas employment of the *tridentate* chelate terpy leads to the isolation of the dinuclear complex **3** with an 1:1 Ga^{III}: ligand ratio. Second, the appearance of HNO_3 in the products might imply that the complexes (which contain hydroxo ligands) would decomposed under "acidic" conditions. We had such an evidence indeed. Complexes **1** and **2** are isolated *only* in the presence of an excess of the heterocyclic ligand (see Section 2). The "stoichiometric" 2:1 (4:2) bpy or phen to Ga^{III} reaction ratio gives solids of uncertain nature with poor analytical results and non-reproducible IR and ^{1}H NMR spectra. We believe that the excess of the organic ligand (which is a Lewis base) neutralizes the nitric acid produced in the reaction and, thus, the latter does not decompose the hydroxo complexes. In the case of **3**, the stoichiometric amount (i.e. terpy: Ga^{III} = 1:1) does not prove detrimental to the formation of the product. However, the yield is low (~25%). The use of an excess of terpy increases the yield (~50%, see Experimental). Third, the weak coordination ability of NO_3^- seems to be responsible for the isolation of cationic complexes; despite our intense efforts (lower *N*-heterocycle: Ga^{III} reaction ratio, use of other-less polar- solvents, refluxing conditions), we could not isolate species containing coordinated nitrates. Fourth, complexes **1**–**3** seem to be the only isolable products from the $Ga(NO_3)_3 \cdot 9H_2O$/bpy, phen or terpy reaction systems in MeOH or MeOH/EtOH. The metal to ligand reaction ratio, the presence of a classical counter-anion (e.g. ClO_4^-) and the precipitation method have no influence on the identity of the products (IR

evidence). For example, use of a large excess of the organic ligand, e.g. 4:1 ligand to metal ratios, does not lead to nitrate salts of the cations $[Ga(bpy)_3]^{3+}$, $[Ga(phen)_3]^{3+}$ or $[Ga(terpy)_2]^{3+}$. It should be stressed at this point that the $[Ga(phen)_3]^{3+}$ and $[Ga(terpy)_2]^{3+}$ cations are not known in the literature. The high yield formation of the salt $[Ga(bpy)_3][I]_3$ was reported two years ago [32] and, surprisingly, still remains the only structurally authenticated example of a homoleptic 2,2′-bipyridine complex of any group 13 element. This salt was unexpectedly prepared by the reaction of "GaI" with one equivalent of bpy in toluene at −78 °C, followed by recrystallization from MeCN; the reaction proceeds via a disproportionation process as evidenced by the deposition of considerable Ga metal from the reaction mixture [32]. And fifth, the full synthetic investigation of the $Ga(NO_3)_3 \cdot 9H_2O$/bpy, phen or terpy reaction systems in MeCN, Me_2CO or DMF led to non-crystalline solids with non-reproducible analytical results. It is remarkable, in this respect, that the complexes $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 5H_2O$ and $[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 4H_2O$ [28], mentioned in Section 1, have been prepared in $MeNO_2$ under gentle heating.

3.2. Description of structures

Partially labelled plots of the dinuclear cations present in complexes **2** · 4.5MeOH, **3** and **1** · 1.3MeOH · 1.4H_2O are shown in Figs. 1, 2, and 4, respectively. A portion of the H-bonded chain that forms in complex **3** is illustrated in Fig. 3. Selected interatomic distances and angles for complexes **2** · 4.5MeOH and **3** are listed in Tables 2 and 3, respectively, while few data for complex **1** · 1.3MeOH · 1.4H_2O are incorporated in Table 4.

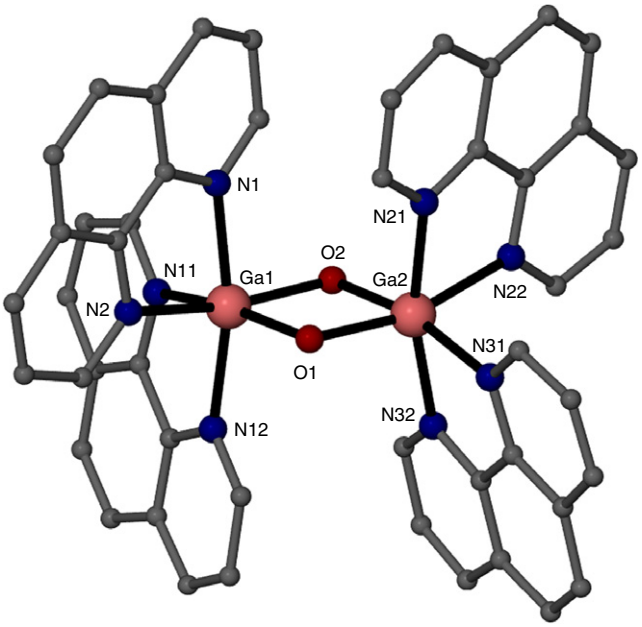

Fig. 1. Partially labelled plot of the cation present in complex **2** · 4.5MeOH.

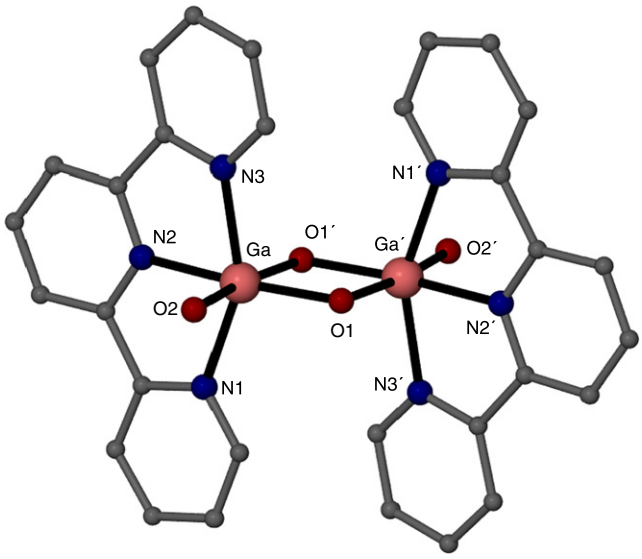

Fig. 2. Partially labelled plot of the cation present in complex **3**. Primed and unprimed atoms are related by the crystallographic inversion centre.

The crystal structure of **2** · 4.5MeOH consists of discrete dinuclear $[Ga_2(OH)_2(phen)_4]^{4+}$ cations, nitrate counteranions and solvate molecules; the latter two will not be further discussed. The two Ga^{III} atoms are doubly bridged by the oxygen atoms (O(1), O(2)) of the two hydroxo ligands. Four nitrogen atoms from two chelating phen molecules complete six-coordination at each metal centre. The presence of two monoatomic bridges causes the Ga(1)···Ga(2) distance to be relatively short (3.007(1) Å). The Ga–O distances are in the relatively narrow range 1.916(3)–1.938(3) Å; such values, as well as the Ga–O–Ga angles (average value 102.9(2)°), are typical for six-coordinate gallium(III) complexes containing the $\{Ga_2^{III}(\mu\text{-}OH)_2\}^{4+}$ core [28,32]. The average Ga–N bond length, 2.086(4) Å, is typical for six-coordinate Ga^{III}/phen complexes [33–36]. There are no significant differences in the lengths of the Ga–N bonds that are *trans* to a nitrogen or oxygen atom. The geometry around the Ga^{III} centres is distorted octahedral; the distortions from a perfect octahedral geometry are primarily consequences of (i) the small bite-angle of the chelating phen ligands, which leads to rather acute N–Ga–N angles in the range 78.2(2)–79.2(2)°, and (ii) the rather small O(1)–Ga(1,2)–O(2) angles (77.0(1), 77.3(1)°).

The crystal structure is stabilized by interionic hydrogen bonds, each hydroxo oxygen atom acting as donor with the nitrate oxygen atoms O(4) and O(9) as acceptors. Their dimensions are: O(1)···O(4) 2.860(8) Å, H(O1)···O(4) 2.14(6) Å, O(1)–H(O1)···O(4) 156(6)° and O(2)···O(9) ($-x+1$, $-y+1$, $-z+1$) 2.711(10) Å, H(O2)···O(9) ($-x+1$, $-y+1$, $-z+1$) 1.95(7), O(2)–H(O2)···O(9) ($-x+1$, $-y+1$, $-z+1$) 164(6)°. Since the methanol hydrogen atoms of this complex were not located by difference maps we cannot comment on other, possible hydrogen

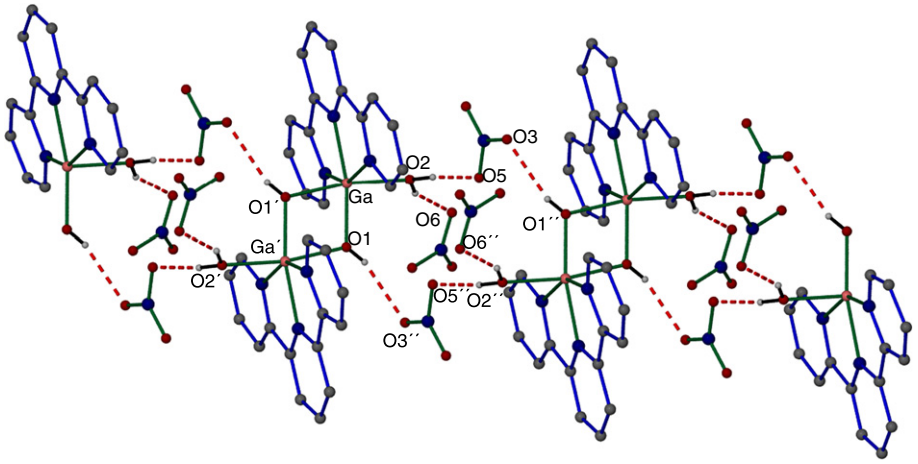

Fig. 3. A small portion of the double, H-bonded chain present in complex **3**. Singly and doubly primed atoms are generated by the symmetry operations $(-x+2, -y+1, -z)$ and $(-x+2, -y+1, -z+1)$, respectively.

Table 2
Selected interatomic distances (Å) and bond angles (°) for complex **2** · 4.5MeOH

Ga(1)···Ga(2)	3.007(1)	Ga(2)–O(1)	1.923(3)
Ga(1)–O(1)	1.938(3)	Ga(2)–O(2)	1.919(3)
Ga(1)–O(2)	1.916(3)	Ga(2)–N(21)	2.101(4)
Ga(1)–N(1)	2.078(4)	Ga(2)–N(22)	2.095(4)
Ga(1)–N(2)	2.096(4)	Ga(2)–N(31)	2.074(4)
Ga(1)–N(11)	2.080(4)	Ga(2)–N(32)	2.089(4)
Ga(1)–N(12)	2.074(4)		
Ga(1)–O(1)–Ga(2)	102.4(2)	Ga(1)–O(2)–Ga(2)	103.3(2)
O(1)–Ga(1)–O(2)	77.0(1)	O(1)–Ga(2)–O(2)	77.3(1)
O(1)–Ga(1)–N(1)	97.6(1)	O(1)–Ga(2)–N(21)	91.1(1)
O(1)–Ga(1)–N(2)	93.6(1)	O(1)–Ga(2)–N(22)	164.5(1)
O(1)–Ga(1)–N(11)	166.0(1)	O(1)–Ga(2)–N(31)	97.0(1)
O(1)–Ga(1)–N(12)	90.5(1)	O(1)–Ga(2)–N(32)	100.6(1)
O(2)–Ga(1)–N(1)	89.3(1)	O(2)–Ga(2)–N(21)	98.4(1)
O(2)–Ga(1)–N(2)	163.4(1)	O(2)–Ga(2)–N(22)	93.0(1)
O(2)–Ga(1)–N(11)	95.6(1)	O(2)–Ga(2)–N(31)	167.6(1)
O(2)–Ga(1)–N(12)	101.3(1)	O(2)–Ga(2)–N(32)	91.2(1)
N(1)–Ga(1)–N(2)	78.3(1)	N(21)–Ga(2)–N(22)	78.2(1)
N(1)–Ga(1)–N(11)	94.1(2)	N(21)–Ga(2)–N(31)	92.7(1)
N(1)–Ga(1)–N(12)	167.9(1)	N(21)–Ga(2)–N(32)	166.3(1)
N(2)–Ga(1)–N(11)	96.2(1)	N(22)–Ga(2)–N(31)	94.8(1)
N(2)–Ga(1)–N(12)	92.4(1)	N(22)–Ga(2)–N(32)	91.5(1)
N(11)–Ga(1)–N(12)	79.2(2)	N(31)–Ga(2)–N(32)	79.0(1)

Table 3
Selected interatomic distances (Å) and bond angles (°) for complex **3**

Ga···Ga′	3.056(1)	Ga–N(1)	2.089(2)
Ga–O(1)	1.893(2)	Ga–N(2)	2.028(2)
Ga–O(1′)	1.972(2)	Ga–N(3)	2.117(2)
Ga–O(2)	1.969(2)		
Ga–O(1)–Ga′	104.5(1)	O(1′)–Ga–N(2)	92.6(1)
O(1)–Ga–O(1′)	75.5(1)	O(1′)–Ga–N(3)	94.3(1)
O(1)–Ga–O(2)	95.4(1)	O(2)–Ga–N(1)	88.3(1)
O(1)–Ga–N(1)	103.7(1)	O(2)–Ga–N(2)	96.6(1)
O(1)–Ga–N(2)	168.1(1)	O(2)–Ga–N(3)	88.0(1)
O(1)–Ga–N(3)	103.2(1)	N(1)–Ga–N(2)	77.0(1)
O(1′)–Ga–O(2)	170.9(1)	N(1)–Ga–N(3)	153.1(1)
O(1′)–Ga–N(1)	93.7(1)	N(2)–Ga–N(3)	77.0(1)

Primed atoms are related to the unprimed ones by the symmetry transformation $-x+2, -y+1, -z$.

bonds. However, some O(methanol)···O(nitrate) and O(methanol)···O(methanol) distances in the range 2.80–3.15 Å may suggest extra hydrogen bonding. The crystal structure is further stabilized by one type of intermolecular π–π stacking interactions. The interaction involves the pyridine rings that possess atoms N(2) and N(22) $(x-1, y, z)$, the centroid···centroid distance being 3.72 Å. The two rings are almost parallel (dihedral angle 1.0°) and this interaction creates 1D "chains".

Complex **2** · 4.5MeOH joins only a handful of structurally characterized, non-organometallic Ga^{III}/phen complexes [33–36].

Complex **3** crystallizes in triclinic space $P\bar{1}$ Its structure consists of centrosymmetric dinuclear $[Ga_2(OH)_2(H_2O)_2(terpy)_2]^{4+}$ cations and nitrate anions; the latter will not be further discussed. The two Ga^{III} atoms are doubly bridged by the hydroxo oxygen atoms O(1) and O(1′), while one tridentate chelating terpy molecule and one aquo ligand complete six-coordination at each metal centre. The GaO(1)Ga′O(1′) core is strictly planar due to the presence of the inversion centre in the middle of the core, with a Ga–O(H)–Ga′ angle of 104.5(1)° and a Ga···Ga′ separation of 3.056(1) Å. The hydroxo bridge is slightly asymmetric, with the Ga–O(1) and Ga′–O(1) bond lengths being 1.893(2) and 1.972(2) Å, respectively. The geometry about the metal ion is distorted octahedral. The "*trans*" N(1)–Ga–N(3) angle (153.1(1)°) deviates significantly from the ideal value of 180°. The terpy ligand occupies meridional sites and exhibits the expected *cisoid* conformation about the interannular C–C bonds, necessary for the adoption of the chelating mode.

The Ga–N bond lengths (2.028(2)–2.117(2) Å) are very close to those in the other two structurally characterized, six-coordinate Ga^{III}/terpy complexes, i.e. $[Ga(OH)(SO_4)(terpy)(H_2O)] \cdot H_2O$ [24] and $[GaCl_3(terpy)]$ [37]. The Ga–N contact to the central ring of the terpy ligand (Ga–N(2), 2.028(2) Å) is shorter than the Ga–N contacts to the terminal rings (Ga–N(1), 2.089(2) Å; Ga–N(3),

Table 4
Selected structural parameters for the structurally characterized complexes containing the cation $[Ga_2(\mu\text{-}OH)_2(bpy)_2]^{4+}$

Complex	$Ga^{III}\cdots Ga^{III}$(Å)	Ga–O[a](Å)	Ga–N[a](Å)	Ga–O–Ga[a](°)	Ref.
$[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 4H_2O$	3.017	1.913	2.103	104.1	[28]
$[Ga_2(OH)_2(bpy)_4](NO_3)_4 \cdot 5H_2O$	3.003	1.923	2.067	102.9	[28]
$\{[Ga_2(OH)_2(bpy)_4]\}_2[Ga_2^{II}I_6][I]_6$	3.035	1.941	2.078	102.9	[32]
$[Ga_2(OH)_2(bpy)_4][I]_4$	3.058	1.948	2.071	103.4	[32]
1 · 1.3MeOH · $1.4H_2O$	3.027	1.929	2.077	103.4	This work

[a] Mean values.

2.117(2) Å), as observed in other complexes containing tridentate terpy ligands [24,37–39]. The bond distances and angles within the terpy ligands are typical [24,37–39]. The three pyridine rings are not exactly planar, and the two N(1)- and N(3)-containing terminal rings make least-squares plane angles of 2.4 and 5.1°, respectively, with the central ring. A slightly distortion from planarity is common to complexed terpy [24,38–41].

Compound **3** is hydrogen bonded. The aqua and hydroxo oxygen atoms are involved as donors, while the nitrate atoms O(3), O(5), and O(6) act as acceptors (Fig. 3). The metric parameters are: $O(1)\cdots O(3'')$ $(-x+2,-y+1,-z+1)$ 2.854(3) Å, $H(O1)\cdots O(3'')$ $(-x+2, -y+1,-z+1)$ 2.18(3) Å, $O(1)\text{–}H(O1)\cdots O(3'')$ $(-x+2,-y+1,-z+1)$ 162(4)°; $O(2)\cdots O(5)$ 2.651(4) Å, $H_A(O2)\cdots O(5)$ 1.77(5) Å, $O(2)\text{–}H_A(O2)\cdots O(5)$ 175(2)°; $O(2)\cdots O(6)$ 2.633(5) Å, $H_B(O2)\cdots(O6)$ 1.99(4) Å, $O(2)\text{–}H_B(O2)\cdots O(6)$ 154(4)°. The $O(2)\text{–}H_A(O2)\cdots O(5)$ and $O(1)\text{–}H(O1)\text{–}O(3'')$ $(-x+2, -y+1,-z+1)$ hydrogen bonds (and their symmetry partners) create a double-chain, ladder-like architecture (Fig. 3). Contrary to the two just mentioned hydrogen bonds, the third $O(2)\text{–}H_B(O2)\cdots O(6)$ hydrogen bond does not contribute to the chain formation. There are no π–π stacking interactions in the crystal structure.

The molecular structure of the cation $[Ga_2(\mu\text{-}OH)_2(bpy)_4]^{4+}$ of complex **1** · 1.3MeOH · $1.4H_2O$ is similar in almost all aspects with that of the cation of **2** · 4.5MeOH, the only essential difference being the fact that the cation of the former lies on a crystallographic twofold axis (Fig. 4). Obviously, the replacement of phen by bpy has little structural effect. Thus, the structure of **1** · 1.3MeOH · $1.4H_2O$ will not be discussed in detail. Complex **1** joins a small family of structurally characterized homometallic Ga^{III}/bpy complexes [9,28,32,42–44].

Complex **1** extends to five the number of structurally characterized gallium(III) compounds that contain the cation $[Ga_2(\mu\text{-}OH)_2(bpy)_4]^{2+}$. Since the four other compounds were reported only recently, we felt it timely to collect the salts that contain this dinuclear cation in Table 4, together with some typical structural parameters. The remarkable similarity of the molecular structures is clearly evident; moreover, the angular geometries of the Ga^{III} atoms are closely similar. For this reason we have not included in this paper a full table with selected interatomic distances angles for **1** · 1.3MeOH · $1.4H_2O$.

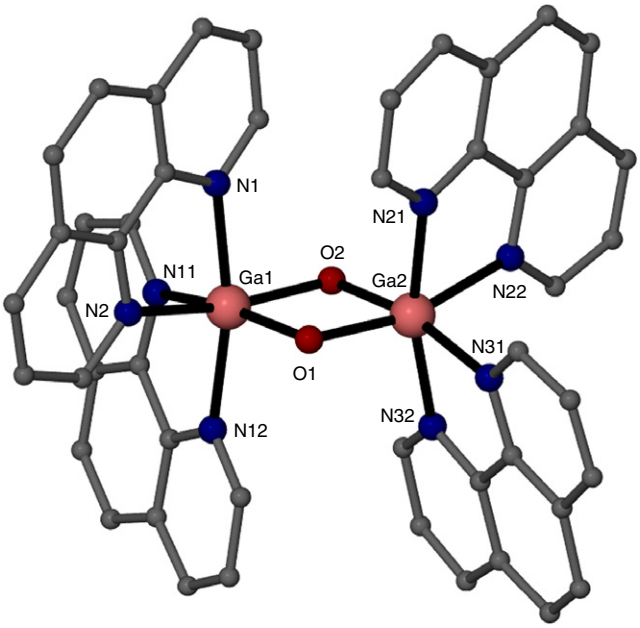

Fig. 4. Partially labelled plot of the cation present in complex **1** · 1.3MeOH · $1.4H_2O$. Primed atoms are related to the unprimed ones by the symmetry transformation $-x, y, -z+1/2$.

3.3. Spectroscopic characterization

The IR spectrum of **3** exhibits a medium intensity band at ~3440 cm^{-1}, assignable to $\nu(OH)_{coord.\,water}$ [45]. The ν(OH) vibration of the lattice H_2O appears as a shoulder at 3310 cm^{-1} in the IR spectrum of a dried sample of **1** · H_2O [45]. The presence of hydroxo ligands in **1**–**3** is manifested by a medium to strong intensity band at 3418–3508 cm^{-1} [46]. The broadness and relatively low frequency of the water and hydroxo bands are indicative of hydrogen bonding.

The existence of ionic nitrates (point–group D_{3h}) in **1**–**3**, established crystallographically, is reflected in the appearance of a strong band at ~1385 cm^{-1}, which is assigned to the $\nu_3(E')(\nu_d(NO))$ vibrational mode [47].

The ν(C⋯C) and ν(C⋯N) bands of bpy in the 1600–1400 cm^{-1} region are sensitive to chelation [48,49]. The 1578 and 1556 cm^{-1} bands of free bpy shift to higher wavenumbers with simultaneous splitting in **1**; a higher wavenumber shift is also observed for the bands at 1452 and 1414 cm^{-1} which appear at 1480 and 1448 cm^{-1}, respectively, in the spectrum of the complex. Other characteristic

vibrations of free bpy are the C–H out-of-plane deformations which appear as a strong band at 756 cm^{-1} and a weak satellite at 739 cm^{-1}; upon chelation two strong bands at 768 and 730 cm^{-1} are observed [49]. Bands of phen in the 1630–1400 cm^{-1} region, attributed to ring stretching vibrations, shift to higher wavenumbers upon chelation [49,50] in **2**. Similar shifts occur for the bands between 1250 and 1100 cm^{-1}, while those between 1050 and 700 cm^{-1} shift to lower frequencies with splitting of the two strong bands at ca. 850 and 720 cm^{-1} (out-of-plane C–H deformations) [49]. Two groups of very intense bands assigned to ν(C⋯N) and ν(C⋯C) appear at 1582–1560 and 1478–1422 cm^{-1} for free terpy [24,51]. The two bands of the first group show a ~20 cm^{-1} shift to higher frequencies in **3** due to coordination [24]. The second group shows a shift to higher wavenumbers and also a splitting [24].

The ^{1}H NMR spectra of complexes **2** and **3** in DMSO-d_6 and D_2O are indicative of the presence of free ligand (phen and terpy, respectively) and one solution species containing the coordinated ligand, indicating that the structures of the complexes are not retained in solution. For this reason, we did not proceed to a detailed ^{1}H NMR study of the two complexes. Thus, for example, the spectrum of **2** in D_2O consists of eight resonances. Four of the signals appear at exactly the same δ values as for free phen [49]. Using the classical numbering scheme of 1,10-phenanthroline the signals at δ 9.17, 7.65, 8.47, and 7.81 ppm, are assigned to protons H(2,9), H(3,8), H(4,7) and H(5,6), respectively [52]. The corresponding signals for the coordinated phen appear at δ 8.90, 7.71, 8.74, and 8.25 ppm. We believe that the solution complex species contains two phen molecules per Ga^{III} atom. Our argument, supported by literature reports [52], is the following: The close proximity of two phen ligands in the first coordination sphere of the metal ion in the 1:2 complex should result in shielding effects due to mutual diamagnetic anisotropy of the aromatic rings; these effects should be absent in the 1:1 complex. This anisotropic contribution should be more effective with a decrease in the distance between the two phen moieties, so that the corresponding contribution for each proton would be in the order H(2,9) > H(3,8) > H(4,7) > H(5,6). This is exactly what is experimentally observed.

The singlet peak at δ 2.03 in the ^{1}H NMR spectrum of **1** in DMSO-d_6 can be assigned to the bridging hydroxo groups [32]. The ^{1}H NMR spectrum in D_2O consists of four doublet signals and three triplet signals. Data (TMS, δ): 8:90 (d, 1H, A), 8.75 (d, 1H, B), 8.55 (t, 1H, C), 8.38 (d, 1H, D), 8.37 (t, 1H, E), 8.33 (t, 1H, F), 7.56 (d, 1H, G) and 7.51 (t, 1H, H). The ^{1}H NMR assignments of the aromatic protons in D_2O have been achieved by a 2D COSY experiment which unravels the connectivities among the adjacent protons. Adopting the bpy numbering scheme presented in Fig. 5, each bpy molecule should exhibit two doublet signals for the protons H(3) and H(6), and two triplet signals for the protons H(5) and H(6). If complex **1** did not have symmetry elements in solution, it would feature four non-equivalent bpy ligands. Then eight doublets and eight triplets would have been observed in the ^{1}H NMR spectrum. However, only four doublet and four triplet signals for the four coordinated bpy ligands are observed, indicating an equivalence of these bipy molecules that can only be explained by the

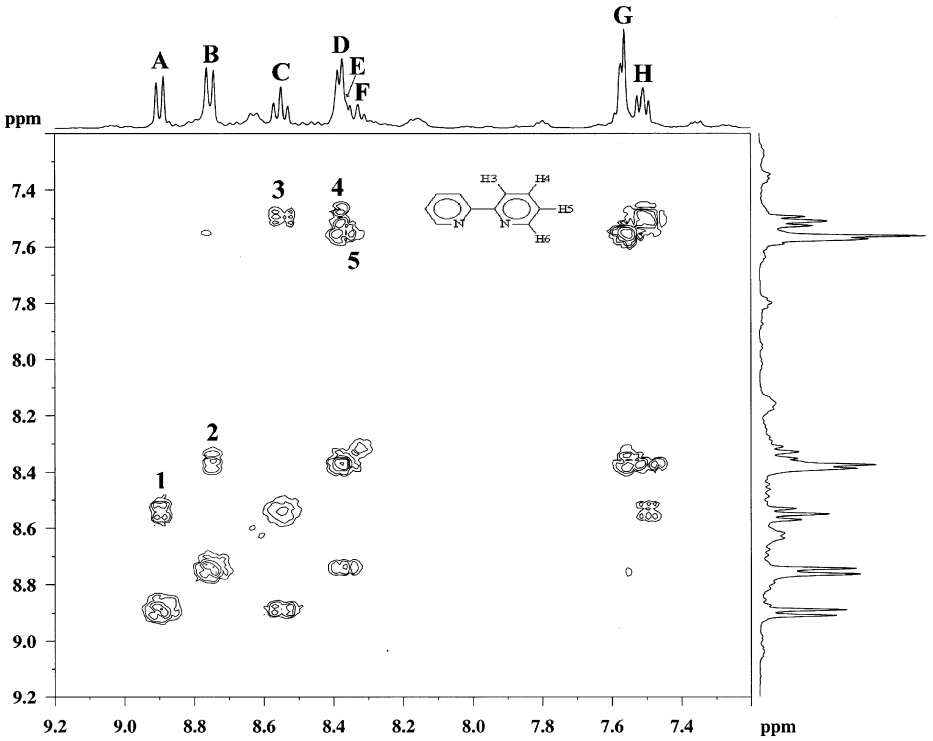

Fig. 5. The room-temperature 2D homonuclear COSY map of complex **1** in D_2O.

presence of an overall 2-fold symmetry in solution, which is also present in the solid state (see Part 3.2). Each pair of the equivalent bpy ligands exhibits a group of two doublet (H(3) and H(6)) and two triplets (H(4) and H(5)). This conclusion is supported by the fact that the chemical shifts of each group do not feature connectivities with the chemical shifts of the other group in the COSY map.

The 2D homonuclear COSY map of **1** in D_2O is shown in Fig. 5. We observe cross-peaks between the signals A and C, C and H, and H and D (cross-peaks 1, 3 and 4, respectively). These signals are due to the first pair of the equivalent bpy ligands. The cross-peaks between the signals B and E, and F and G (cross-peaks 2 and 5, respectively) are due to the second pair of equivalent bpy ligands. Unfortunately, we cannot observe the expected cross-peaks between the signals E and F which are overlapped. In the first group of signals, the signal A at the higher δ value can assigned to H(6), which is very close to the nitrogen atom and the metal ion. Signals C, H and D are therefore assigned to protons H(5), H(4) and H(3), respectively. In the second group of signals, signal B is assigned to H(6*) (the asterisk denotes the second pair of equivalent bpy ligands) and therefore signal E to H(5*). We are thus left with the two unassigned signals F and G. Since we have observed a cross-peak between them, and by exclusion, we assign the signals F and G to protons H(4*) and H(3*), respectively.

4. Conclusions and perspectives

The $Ga(NO_3)_3$/bpy, phen and terpy reaction systems have fulfilled their promise as a source of interesting complexes containing the $Ga^{III}{}_2(\mu\text{-}OH)_2\}^{4+}$ core. Under the reaction conditions employed, the nitrates are not coordinated to gallium(III); this consideration will be important as this work is extended to other *N*-heterocyclic ligands. It should be mentioned at this point that the $Ga(NO_3)_3$/bpy system is synthetically different from the $Ga(NO_3)_3$/dmbpy reaction system (dmbpy = 4,4′-dimethyl-2,2′-bipyridine); we have recently shown [25] that the reaction of $Ga(NO_3)_3 \cdot 9H_2O$ with dmbpy in $MeOH/Me_2CO$ leads to the complex *cis*-$[Ga(H_2O)_2(dmbpy)_2](NO_3)_3$.

The terminal aqua ligands that are present in **3** could have future utility as sites for facile incorporation of other neutral or anioning monodentate ligands by metathesis or as a means of accessing higher-nuclearity hydroxo species by using bis(monodentate) bridging ligands. We are also using substituted terpy molecules as terminal ligands in gallium(III) nitrate chemistry to prepare other types of complexes and to control the assembly of polynuclear complexes possessing specific spatial properties. The study of the antitumour properties of **1-3** is also in progress.

5. Supplementary data

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) quoting the deposition numbers 603233 (**1** · 1.3MeOH · 1.4H_2O), 603234 (**2** · 4.5MeOH) and 603235 (**3**).

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