

Mononuclear gallium(III) complexes based on salicylaldoximes: Synthesis, structure and spectroscopic characterization

Christiana Birnara^a, Vadim G. Kessler^b, Giannis S. Papaefstathiou^{a,*}

^aLaboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Zografou 157 71, Greece

^bDepartment of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015, 750 07 Uppsala, Sweden

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Dedicated to Dr. Aris Terzis on the occasion of his retirement and for advancing inorganic chemistry in Greece through X-ray crystallography.

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ABSTRACT

The reactions of Ga(acac)₃ with salicylaldoxime (saoH₂) and methyl-salicylaldoxime (Me-saoH₂) in dichloromethane/hexane afforded the complexes [Ga(acac)(saoH)₂] (**1**) and [Ga(acac)₃][Ga(acac)(Me-saoH)₂] (**2**), respectively, in high yields. The crystal structures of **1** and **2** have been determined by single-crystal X-ray crystallography. Both complexes are mononuclear with the Ga(III) atoms being in octahedral environments surrounded by two bidentate chelate R-saoH⁻ and one bidentate chelate acac⁻ ligands. A [Ga(acac)₃] moiety has co-crystallized along with the methylsalicylaldoximate complex. Characteristic IR as well as NMR data are discussed in terms of the nature of bonding in the structures of the two complexes. ¹H and ¹³C NMR data in CDCl₃ indicate that the salicylaldoximate complexes isomerize in solution.

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1. Introduction

Over the last decade the coordination chemistry of salicylaldoxime (saoH₂) and its derivatives (R-saoH₂) (Fig. 1) has attracted a tremendous interest due to the ability of the dianions of those ligands to produce high nuclearity metal complexes especially with trivalent metal ions [1–23]. Besides the intriguing structures of the salicylaldoximate metal clusters, the most remarkable results originate from the magnetic properties of those complexes. It has been discovered that salicylaldoximes may be utilized to produce families of hexanuclear and trinuclear Mn^{III} single-molecules magnets (SMMs) of general formulae [Mn₆^{III}O₂(R-sao)₆(O₂CR)₂(L)_{4–6}] and [Mn₃^{III}O(R-sao)₃(O₂CR)(L)₃] (R = H, Me, Et, etc.; L = solvent) [11–14]. It has also been demonstrated that in each case, by using derivatised versions of the oxime ligand, it was possible to significantly increase the ground spin state from *S* = 4 to *S* = 12 in the former and from *S* = 2 to *S* = 6 in the latter, enhancing the effective energy barrier for magnetization reversal to record levels [11–13].

Inspired by the work of Brechin, Milios and Perlepes involving the synthesis and characterization of Mn(III) and Fe(III) salicylaldoximate clusters [1–16] and given the preference of the salicylaldoximes to coordinate to trivalent metal ions we decided to initiate a project to study the coordination chemistry of salicylaldoximes with Ga(III) aiming to produce diamagnetic analogs of

the already known high nuclearity and/or different nuclearity clusters. Our interest in Ga(III) chemistry [24–29] stems from the fact that some gallium(III) complexes have emerged as leading materials for optoelectronic devices such as light-emitting diodes (LEDs) and laser diodes in the blue/UV region [30,31] as well as potential metallo-drugs mainly due to their antiproliferative activity [32–34].

Herein, we report our first efforts toward the synthesis and characterization of Ga(III) complexes with salicylaldoximes. To this end, we synthesized and characterized by X-ray crystallography, IR, ¹H and ¹³C NMR spectroscopy two new mononuclear Ga^{III} complexes namely [Ga(acac)(saoH)₂] (**1**) and [Ga(acac)₃][Ga(acac)(Me-saoH)₂] (**2**) (acacH = acetylacetone, saoH₂ = salicylaldoxime and Me-saoH₂ = methylsalicylaldoxime). Complexes **1** and **2** represent the second and third salicylaldoximate Ga(III) complexes [35].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions. Gallium metal, acetylacetone, salicylaldehyde, 2'-hydroxyacetophenone, hydroxylamine hydrochloride, sodium carbonate and all solvents were obtained from commercial sources and used as received. Microanalyses (C, H and N) were performed with an EA 1108 Carlo Erba analyzer. IR spectra were recorded on a Perkin-Elmer 880 IR spectrometer with samples prepared as KBr pellets.

* Corresponding author. Tel.: +30 210 727 4840; fax: +30 210 727 4782.

E-mail address: gspapaef@chem.uoa.gr (G.S. Papaefstathiou).

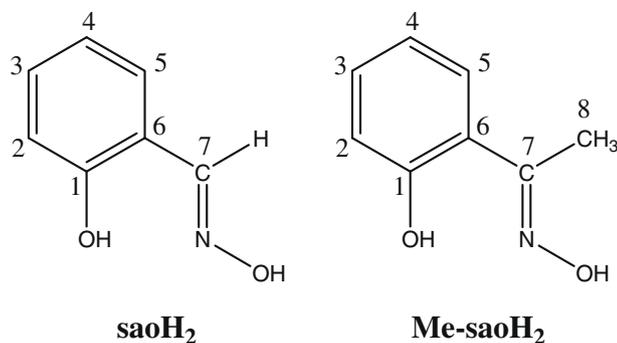


Fig. 1. The structures of the ligands discussed in the text.

^1H and ^{13}C NMR spectra were recorded on a Varian UNITY Plus spectrometer operating at 300 MHz. Samples were run in a 5 mm probe with CDCl_3 as internal lock and reference.

2.2. Compound preparation

2.2.1. Synthesis of $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ga}(\text{acac})_3$

A drop of gallium metal (5.808 g, 83.3 mmol) was weighed in a 100 mL flat bottom flask. Concentrated HNO_3 (65%, 50 mL) was added and the mixture was stirred overnight at room temperature to produce a clear colorless solution. The solution was cooled at 5°C and seeded with a small crystal of $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Almost immediately the whole mass of the solution transformed to a white crystalline solid. The solid was crashed with a glass rod and $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ isolated by vacuum filtration, washed two times with ice-cold water (2×3 mL) and dried over CaCl_2 . Yield: 25.8 g, 74% based on Ga. The filtrate, including the washing liquids, was transferred to a 250 mL flat bottom flask and diluted with water to a final volume of 100 mL. The pH of the solution was adjusted to $\sim 2\text{--}3$ with concentrated NH_3 (25%) and then acacH (26.7 mL, 25.9 mmol) was added. The mixture was heated to reflux while concentrated NH_3 was added in drops until no obvious turbidity was observed by adding. $\text{Ga}(\text{acac})_3$ was separated as a pale white crystalline solid. The pH of the final solution was $\sim 7\text{--}8$. The mixture was left to cool at room temperature and then $\text{Ga}(\text{acac})_3$ was isolated by vacuum filtration, washed several times with water and dried over CaCl_2 . Yield: 6.7 g. IR (KBr pellets, cm^{-1}): 2998w, 2966w, 2922w, 1586s, 1532s, 1382sbr, 1278m, 1194w, 1018m, 934m, 795wsh, 776w, 682w, 654w, 582w. The total yield for both $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ga}(\text{acac})_3$ was 96% based on Ga. Both compounds gave satisfactory analytical data. $\text{Ga}(\text{acac})_3$ can be also synthesized by the reaction of an aqua solution of $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 12-fold excess of acacH in the presence of concentrated NH_3 as described above in yields of 80–85%.

2.2.2. Synthesis of saOH_2 and Me-saOH_2

A water solution (20 mL) containing hydroxylamine hydrochloride (1.40 g, 20.0 mmol) and Na_2CO_3 (1.06 g, 10 mmol) was added to a 100 mL flat bottom flask containing salicylaldehyde (2.46 g, 20 mmol). The resulting mixture was stirred for three days. Salicylaldehyde oxime was separated as a white solid. The solid was isolated by vacuum filtration, washed several times with water and dried over CaCl_2 . Yield: 1.84 g, 67%. IR (KBr pellets, cm^{-1}): 3371mbr, 1623msh, 1614s, 1573s, 1492s, 1472m, 1408m, 1396msh, 1390m, 1295msh, 1285s, 1258s, 1120m, 1192m, 1152m, 1113w, 1037w, 989s, 957m, 899s, 856w, 786m, 753m, 739msh, 720m, 696m, 648s, 561m, 470m. Me-saOH_2 was prepared in a similar manner by replacing salicylaldehyde by 2'-hydroxyacetophenone (2.4 mL, 20 mmol). Yield: 2.65 g, 88%. IR (KBr pellets, cm^{-1}): 3343mbr, 1628s, 1610s, 1584s, 1553w, 1539w, 1505s, 1500s, 1465m, 1403sbr, 1367s, 1310m, 1286s, 1250sbr, 1157m, 1124w,

1070w, 1044s, 1015s, 986w, 942s, 848s, 834s, 781sbr, 748sbr, 652sbr, 561m, 510m.

2.2.3. $[\text{Ga}(\text{acac})(\text{saOH}_2)]$ (**1**)

$\text{Ga}(\text{acac})_3$ (0.13 g, 0.35 mmol) and saOH_2 (0.10 g, 0.73 mmol) were dissolved in CH_2Cl_2 (5 mL). The solution was heated gently and hexane (25 mL) was added. The resulting colorless solution was refluxed for 30 min and left undisturbed to cool to room temperature. Colorless crystals of **1** were formed over a period of one day. The crystals were isolated by vacuum filtration, washed with hexane (2×5 mL) and dried in air. Yield: 0.12 g, 77%. Anal. Calc. for $\text{C}_{19}\text{H}_{19}\text{GaN}_2\text{O}_6$: C, 51.74; H, 4.34; N, 6.35. Found: C, 51.78; H, 4.29; N, 6.37%. IR (KBr pellets, cm^{-1}): 3064mbr, 3004w, 1647m, 1595s, 1586ssh, 1552s, 1530s, 1517s, 1465s, 1440s, 1375s, 1350m, 1328m, 1278s, 1195m, 1150m, 1120w, 1013s, 963w, 953w, 930m, 907m, 859w, 806m, 786w, 757s, 740w, 687w, 642m, 599m, 586w, 570w, 548w, 491w, 453m.

2.2.4. $[\text{Ga}(\text{acac})_3][\text{Ga}(\text{acac})(\text{Me-saOH}_2)]$ (**2**)

$\text{Ga}(\text{acac})_3$ (0.12 g, 0.32 mmol) and Me-saOH_2 (0.05 g, 0.33 mmol) were dissolved in CH_2Cl_2 (4 mL). The solution was heated gently and hexane (30 mL) was added. The resulting colorless solution was refluxed for 30 min and left undisturbed to cool to room temperature. Light yellow crystals of **2** were formed over a period of two days. The crystals were isolated by vacuum filtration, washed with hexane (2×5 mL) and dried in air. Yield: 0.09 g, 65%. Anal. Calc. for $\text{C}_{36}\text{H}_{44}\text{Ga}_2\text{N}_2\text{O}_{12}$: C, 51.71; H, 5.30; N, 3.35. Found: C, 51.76; H, 5.27; N, 3.38%. IR (KBr pellets, cm^{-1}): 3050wbr, 2960w, 1593ssh, 1579s, 1555w, 1528s, 1439m, 1400m, 1337s, 1322w, 1303m, 1275m, 1242m, 1192w, 1160w, 1137w, 1130w, 1076w, 1044w, 1019m, 961w, 953w, 928m, 862m, 770m, 763m, 682w, 644w, 617w, 580w, 565w, 480w.

2.3. Single-crystal X-ray crystallography

The data collection for the single crystals of compounds **1** and **2** was carried out at 22°C on a SMART CCD 1k diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation. Complete crystal data and parameters for data collection and processing are reported in Table 1.

The structures were solved by direct methods using SHELXS-86 [36] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [37]. The coordinates of the metal atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Brief synthetic comments

Complexes **1** and **2**, were obtained by the ligand substitution reactions between $\text{Ga}(\text{acac})_3$ (acacH = 2,4-pentanedione) and R-saOH_2 ($\text{R} = \text{H saOH}_2$, $\text{R} = \text{Me Me-saOH}_2$) in CH_2Cl_2 /hexane solutions as crystalline solids. Eq. (1) summarizes the preparation of the representative complex **1**. Altering the $\text{Ga}(\text{acac})_3/\text{saOH}_2$ ratio in the same solvent mixture did not affect the identity of the product but the yield of the reaction. The use of more polar solvents such as alcohols, acetone or acetonitrile resulted in oily products that could not turn to solids by adding hexane or diethylether. In the case of Me-saOH_2 , we were not able to isolate the $[\text{Ga}(\text{acac})(\text{Me-saOH}_2)]$ without the presence of $\text{Ga}(\text{acac})_3$. The use of polar solvents had the same effect as in the case of **1**.

Table 1
Crystallographic data for complexes **1** and **2**.

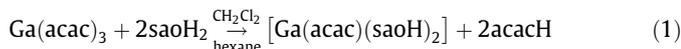
Parameter	1	2
Formula	C ₁₉ H ₁₉ GaN ₂ O ₆	C ₃₆ H ₄₄ Ga ₂ N ₂ O ₁₂
Formula weight	441.08	836.17
Crystal color, habit	colorless, plates	colorless, plates
Crystal dimensions (mm)	0.35 × 0.28 × 0.08	0.30 × 0.28 × 0.08
Crystal system	monoclinic	monoclinic
Space group	<i>P2</i> / <i>c</i>	<i>P2</i> ₁ / <i>n</i>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	13.110(3)	19.366(3)
<i>b</i> (Å)	10.720(2)	8.2867(15)
<i>c</i> (Å)	14.975(4)	23.900(4)
α (°)	90	90
β (°)	112.680(7)	98.736(6)
γ (°)	90	90
<i>V</i> (Å ³)	1941.8(8)	3791.0(12)
<i>Z</i>	4	4
ρ _{calc} (g cm ⁻³)	1.509	1.465
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
<i>T</i> (K)	298(2)	298(2)
θ Range (°)	1.68–23.49	1.26–23.50
μ (mm ⁻¹)	1.455	1.485
Collected reflections	7050	13 970
Independent reflections (<i>R</i> _{int})	2840 (0.0373)	5396 (0.0600)
Observed reflections <i>I</i> > 2σ(<i>I</i>)	2037	3333
Parameters refined	253	469
(Δρ) _{max} , (Δρ) _{min} . (e Å ⁻³)	1.955, -0.655	0.817, -0.716
Goodness-of-fit (GOF) (on <i>F</i> ²)	1.066	0.992
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0946, 0.2081	0.1257, 0.2546
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0687, 0.1966 ^c	0.0728, 0.2058 ^d

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

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

^c For 2037 reflections with *I* > 2σ(*I*).

^d For 3333 reflections with *I* > 2σ(*I*).



3.2. Description of structures

Complex **1** crystallizes in the monoclinic space group *P2*/*c*. The molecular structure of **1** is shown in Fig. 2 while selected bond distances and angles are listed in Table 2. The Ga^{III} ion is in a distorted octahedral geometry. Two saOH⁻ ligands chelate the Ga^{III} ion through the deprotonated phenoxy oxygen atom and the oximic nitrogen atom with the oxygen atoms in *trans* and the nitrogen atoms in *cis* orientation. A bidentate chelate acac⁻ ligand completes the octahedron with both oxygen atoms in *trans* orientation with respect to the oximic nitrogen atoms of the saOH⁻ ligands. The Ga–O_{acac} and Ga–O_{saOH} are very similar ranging from 1.928 to 1.934 Å while the two Ga–N distances are 2.067 and 2.069 Å

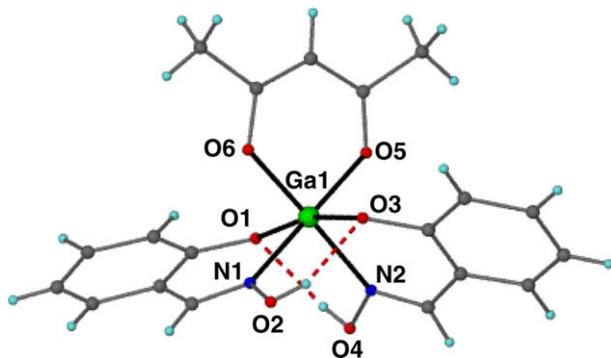


Fig. 2. Ball and stick representation of the molecular structure of **1**.

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

Ga1–O1	1.934(5)	Ga1–O6	1.932(6)
Ga1–O3	1.927(5)	Ga1–N1	2.067(6)
Ga1–O5	1.931(6)	Ga1–N2	2.069(6)
O1–Ga1–O3	166.3(2)	O3–Ga1–N2	86.3(2)
O1–Ga1–O5	95.3(2)	O5–Ga1–O6	92.6(3)
O1–Ga1–O6	91.8(2)	O5–Ga1–N1	178.2(2)
O1–Ga1–N1	85.7(2)	O5–Ga1–N2	86.3(3)
O1–Ga1–N2	84.2(2)	O6–Ga1–N1	89.0(3)
O3–Ga1–O5	94.0(2)	O6–Ga1–N2	175.7(2)
O3–Ga1–O6	97.9(2)	N1–Ga1–N2	92.3(3)
O3–Ga1–N1	84.8(2)		

for Ga1–N1 and Ga1–N2, respectively and compare favorably with those of other octahedral Ga(III) complexes [38]. Each of the two oximic OH groups forms an intramolecular hydrogen bond with the phenoxy oxygen atom of a neighboring saOH⁻ [O2–H2A...O3, O...O 2.643(9) Å and O4–H4A...O1, O...O 2.621(7) Å].

Complex **2** crystallizes in the monoclinic space group *P2*₁/*n*, with two mononuclear complexes in the unit cell, namely [Ga(acac)₃] and [Ga(acac)(Me-saOH)₂]. Fig. 3 shows the asymmetric unit of **2**, while selected bond distances and angles are listed in Table 3. The structure of [Ga(acac)₃] within **2** compares well with the structures of [Ga(acac)₃] [39] and [Ga(acac)₃].*trans*-CHCl=CHCl [40]. The structure of [Ga(acac)(Me-saOH)₂] is very similar to that of **1**. The Ga^{III} ion is in a distorted octahedral geometry with two bidentate chelate Me-saOH⁻ ligands to coordinate through the deprotonated phenoxy oxygen atom and the oximic nitrogen atom around the Ga^{III} ion with the oxygen atoms in *trans* and the nitrogen atoms in *cis* orientation. The acac⁻ ligand chelates the central atom with

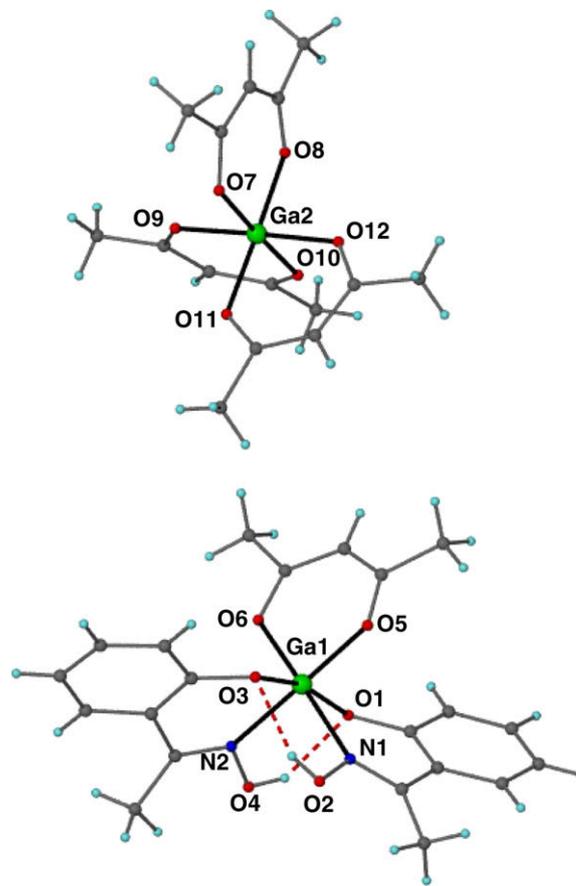


Fig. 3. Ball and stick representation of the asymmetric unit of **2**.

Table 3
Selected bond distances (Å) and angles (°) in **2**.

Ga1–O1	1.920(6)	Ga2–O9	1.925(7)
Ga1–O3	1.901(7)	Ga2–O10	1.947(6)
Ga1–O5	1.935(6)	Ga2–O11	1.938(7)
Ga1–O6	1.932(5)	Ga2–O12	1.935(7)
Ga1–N1	2.112(7)	Ga2–O7	1.938(6)
Ga1–N2	2.069(7)	Ga2–O8	1.953(5)
O1–Ga1–O3	164.6(3)	O8–Ga2–O11	178.9(3)
O1–Ga1–O5	94.4(2)	O8–Ga2–O12	89.3(3)
O1–Ga1–O6	92.8(2)	O9–Ga2–O10	92.5(3)
O1–Ga1–N1	83.2(3)	O9–Ga2–O11	86.4(3)
O1–Ga1–N2	85.3(2)	O9–Ga2–O12	178.1(3)
O3–Ga1–O5	94.2(2)	O10–Ga2–O11	93.2(3)
O3–Ga1–O6	99.5(3)	O10–Ga2–O12	87.3(3)
O3–Ga1–N1	84.1(3)	O11–Ga2–O12	91.7(3)
O3–Ga1–N2	86.4(2)	O8–Ga2–O10	87.3(3)
O5–Ga1–O6	92.6(2)	O7–Ga2–O8	90.9(3)
O5–Ga1–N1	90.1(3)	O7–Ga2–O9	89.4(3)
O5–Ga1–N2	178.6(2)	O7–Ga2–O10	177.5(3)
O6–Ga1–N1	175.4(3)	O7–Ga2–O11	88.6(3)
O6–Ga1–N2	86.1(3)	O7–Ga2–O12	90.9(3)
N1–Ga1–N2	91.3(3)	O8–Ga2–O9	92.6(2)

both oxygen atoms in *trans* orientation with respect to the oximic nitrogen atoms of the Me-saoH[−] ligands. The oximic OH groups form two intramolecular hydrogen bonds with the phenoxy oxygen atoms of the neighboring Me-saoH[−] ligands [O2–H2A...O3, O...O 2.609(8) Å and O4–H4A...O1, O...O 2.589(8) Å].

3.3. Spectroscopic characterization

3.3.1. IR spectroscopy

In the $\nu(\text{O–H})$ region, the IR spectra of the complexes exhibit medium-intensity broad bands at 3064 (**1**) and 3050 (**2**) cm^{-1} , assignable to $\nu(\text{O–H})_{\text{oxime}}$. The broadness and the relatively low frequency of these bands are both indicative of hydrogen bonding. The $\nu(\text{C=N})$ in spectra free ligands appear at 1623 and 1628 cm^{-1} for saoH₂ and Me-saoH₂, respectively. These bands are shifted to lower wavenumbers in the spectra of **1** (1595 cm^{-1}) and **2** (1593 cm^{-1}) due to complexation. The $\nu(\text{C=C})$ and $\nu(\text{C=O})$ modes

of the acetylacetonate ligand at 1586 and 1532 cm^{-1} in the spectrum of Ga(acac)₃ have not shifted significantly in the spectra of **1** (1586 and 1530 cm^{-1}) and **2** (1579 and 1528 cm^{-1}), respectively.

3.3.2. ¹H and ¹³C NMR spectroscopy

¹H and ¹³C NMR spectra of **1**, **2**, Ga(acac)₃, saoH₂ and Me-saoH₂ were recorded in CDCl₃ solution at ambient temperature. Figs. 4, 5 and 7, 8 show the ¹H and ¹³C NMR spectra of **1** and **2**, respectively. The signal assignment is based on chemical shifts and comparison between the spectra of the complexes and the spectra of the starting materials. The ¹H and ¹³C NMR spectra of Ga(acac)₃, saoH₂ and Me-saoH₂ are shown in Figs. S1–S6. The methyl (CH₃) and methinic (CH) protons of the acac[−] ligands in spectrum of Ga(acac)₃ appear as two singlets at 2.01 and 5.44 ppm, respectively (Fig. S1). The spectrum of **1** (Fig. 4) is more complex in these two regions exhibiting three distinct signals (singlets) and a shoulder for each of the methyl and methinic protons of the acac[−] ligand. The oximic (NOH) and the methinic (C–H) protons in the spectrum of saoH₂ appear as two singlets at 10.03 and 8.24 ppm, respectively (Fig. S2). Those signals have shifted downfield in the spectrum of **1** due to the deprotonation and coordination of the saoH[−] ligands and split in sets of two peaks at 9.96 and 9.75 for the oximic and 8.22 and 8.20 for the methinic protons. The phenolic proton (OH) appears as a singlet at 7.86 in the spectrum of saoH₂ and it is absent in the spectrum of **1**. The aromatic protons in the spectrum of saoH₂ appear as two triplets for the C3 and C4 protons and two doublets for C2 and C5 protons (for numbering pattern see Fig. 1). The spectrum of **1** is more complex in the region of the aromatic protons exhibiting not only overlapping signals of triplets and doublets but overlapping of lower integration peaks which indicate the presence of isomers in the CDCl₃ solution.

The ¹³C NMR spectrum of **1** corroborates with the presence of isomers in the CDCl₃ solution (Fig. 5). The methyl (CH₃), methinic (CH) and carbonyl (CO) carbon atoms of the acac[−] ligands appear at 27.36, 100.36 and 192.96 ppm in the spectrum of Ga(acac)₃ (Fig. S3). Those signals have not shifted significantly in the spectrum of **1**, but the signals of the methyl and methinic carbon atoms have split in sets of two signals (Fig. 5). The seven carbon atoms of saoH₂ appear as seven distinct peaks in the ¹³C NMR spectrum of

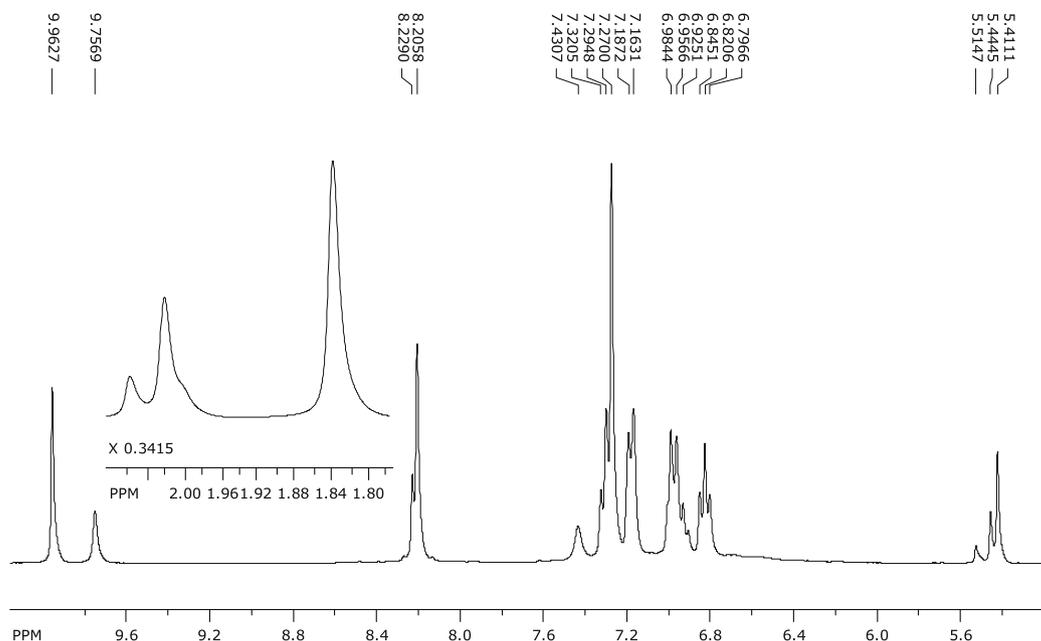


Fig. 4. The ¹H NMR spectrum of **1** in CDCl₃.

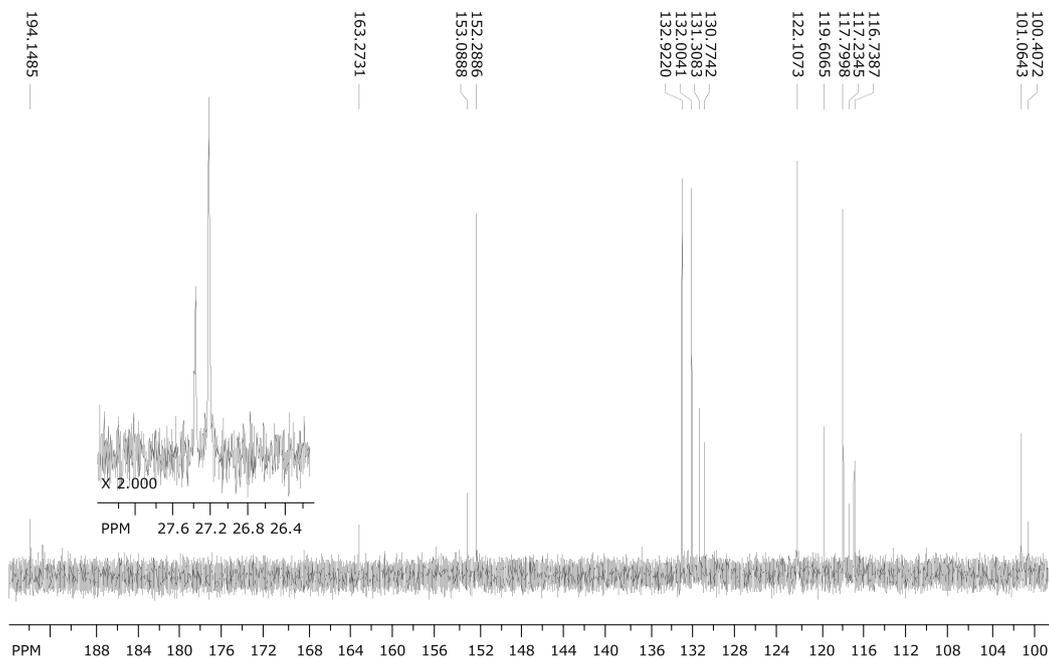


Fig. 5. The ^{13}C NMR spectrum of **1** in CDCl_3 .

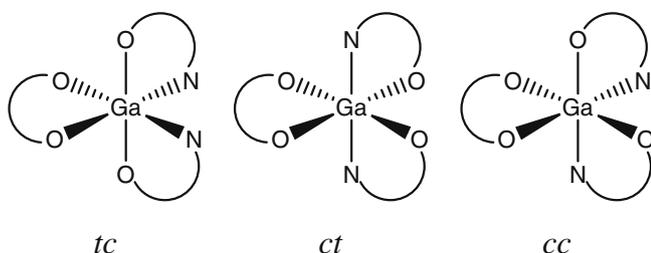


Fig. 6. The structures of the three geometric isomers of the Tris-chelate $[\text{Ga}(\text{O},\text{O})(\text{O},\text{N})_2]$ complexes.

the ligand (Fig. S4). Those peaks have shifted and split in sets of two peaks for all carbon atoms of saoH^- except for the C1 and C6 which appear as two single peaks at 194.14 and 117.23 ppm in the ^{13}C NMR spectrum of **1**, respectively (Fig. 5). The fact that those two carbon atoms as well as the carbonyl carbon atoms of the acac^- ligand give very weak signals in the ^{13}C NMR spectra of saoH_2 and $\text{Ga}(\text{acac})_3$ and given that the minor species of **1** give a small percent signals compared with the signals of the majors species in solution, suggest that the signals of the minor species for those three carbon atoms are within the noise in the spectrum of **1**.

Tris-chelate complexes of the general formula $[\text{Ga}(\text{O},\text{O})(\text{O},\text{N})_2]$ such as **1** and the $[\text{Ga}(\text{acac})(\text{Me-saoH})_2]$ in **2** may exist in three iso-

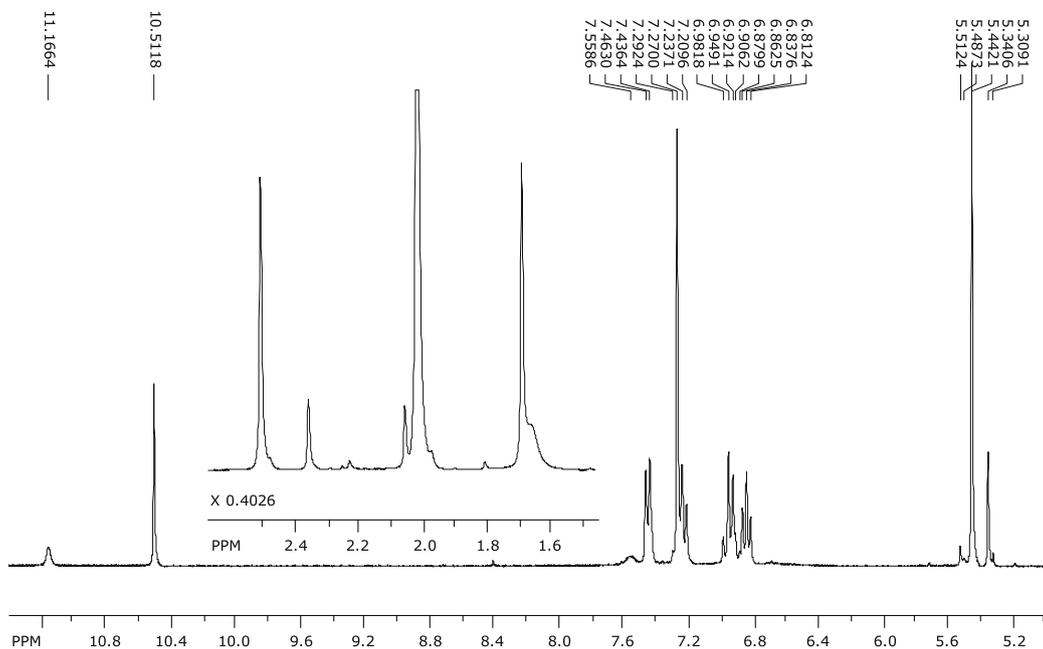


Fig. 7. The ^1H NMR spectrum of **2** in CDCl_3 .

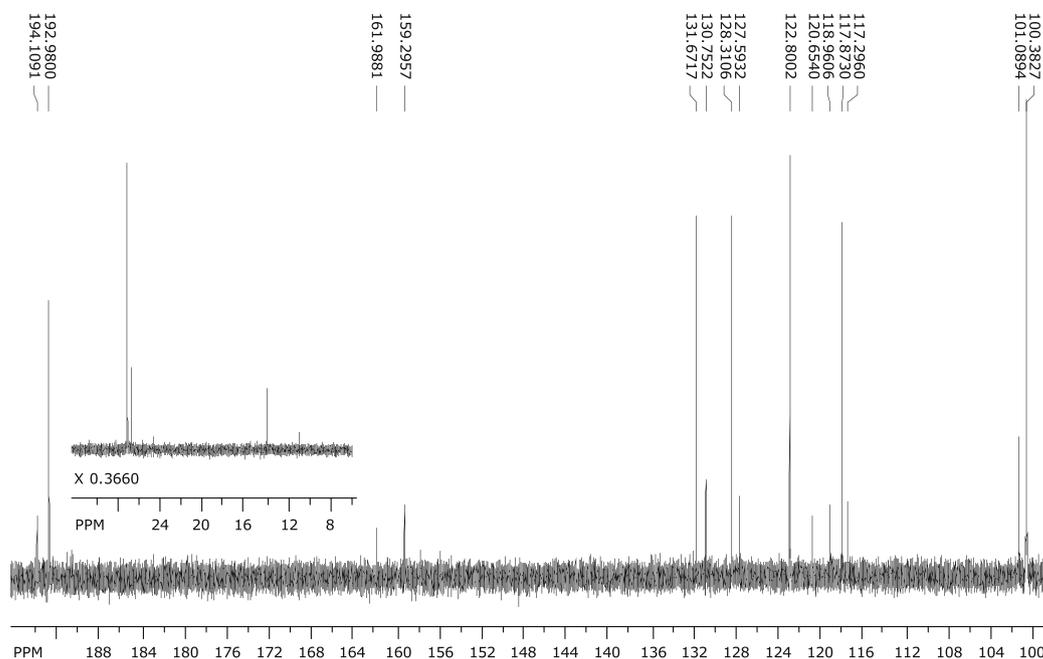


Fig. 8. The ^{13}C NMR spectrum of **2** in CDCl_3 .

meric forms [41–43]. Those three geometric isomers are shown in Fig. 6 and with respect of the orientation of the N and O atoms of the two (O,N)-ligands are the *cis-cis* (*cc*), the *cis-trans* (*ct*) and the *trans-cis* (*tc*) with the latter being the one isolated in the solid-state in **1** and **2**. The *ct* and *tc* isomers have a C_2 -symmetry where as *cc* has a C_1 -symmetry. The ^1H and ^{13}C solution NMR spectra support at least the presence of two isomers in different proportion. The overlapping of the signals in the ^1H NMR spectrum of **1** makes the evaluation of the proportion difficult. A rough estimation of the proportion of the two isomers made on the integration of the oximic (NOH) protons, suggests that the two isomers are present in the CDCl_3 solution in 72:28% ratio.

The ^1H NMR spectrum of **2** indicates the presence of at least two isomers in CDCl_3 solution (Fig. 7). The aliphatic region is more complicated than that in the spectrum of **1** due to the presence of the methyl groups of the $\text{Ga}(\text{acac})_3$ and the Me-saoH^- . The region where the methinic protons of the acac^- ligands appear exhibits five signals, four of which are attributed to the two isomers and one to the methinic proton of the $\text{Ga}(\text{acac})_3$. The aromatic region contains overlapping signals of triplets and doublets as well as lower integration peaks which indicate the presence of the other isomer. A rough estimation of the proportion of the two isomers made again on the oximic protons which appear as two peaks at 10.51 and 11.16 ppm in the spectrum of **2** suggests that the two isomers are present in the CDCl_3 solution in 74:26% ratio, which is similar to that observed in **1**. The ^{13}C NMR spectrum of **2** exhibits two peaks for the Me-saoH^- methyl carbon atoms at 10.76 and 13.81 ppm (Fig. 8). The remaining Me-saoH^- carbon atoms except C1, C6 and C7 (for numbering pattern see Fig. 1) appear as two sets of peaks in the ^{13}C spectrum of **2**, while there are eight distinct signals for the carbon atoms in the ^{13}C NMR spectrum of Me-saoH_2 (Fig. S6). As in the case of **1**, the C1, C6 and C7 atoms give very weak signals in the ^{13}C NMR spectrum of Me-saoH_2 and therefore the signals of the minor species of **2** for those three carbon atoms are not observed. The ^{13}C NMR spectrum of **2** exhibits two peaks for the acac^- methyl carbon atoms around 27 ppm, two peaks for the methinic carbon atom at 100.38 and 101.08 ppm and two peaks for the carbonyl carbon atoms at 194.10 and 192.98 ppm.

A closer look at the spectrum of **2** and the spectrum of $\text{Ga}(\text{acac})_3$ indicates that the higher intensity signals at 27.36, 101.38 and 192.98 ppm are due to the $\text{Ga}(\text{acac})_3$ within **2**. Concentrating our attention at the methinic carbon signals at around 100 ppm in the spectra of **1** and **2**, we can observe that the intense and the weak signals in the spectrum of **1** have been reversed in the spectrum of **2** and that the signals of the minor species in **2** overlap with the signals of the $\text{Ga}(\text{acac})_3$ in **2**.

4. Conclusions and perspectives

Our first attempt to employ salicylaldoximes in the coordination chemistry of Ga(III) afforded two mononuclear Ga(III) complexes. Both complexes were characterized by single-crystal X-ray crystallography, IR, ^1H and ^{13}C NMR spectroscopy. Complex **1** is an octahedral Ga(III) complex surrounded by a bidentate-chelate saoH^- ligand and a bidentate chelate acac^- ligand, while complex **2** contains the same core with Me-saoH^- instead of saoH^- and has co-crystallized with one $\text{Ga}(\text{acac})_3$ molecule. Both ^1H and ^{13}C NMR spectra of the compounds suggest the presence of at least two geometrical isomers in the CDCl_3 solution. Detailed preparations of the starting materials $\text{Ga}(\text{acac})_3$, saoH_2 and Me-saoH_2 as well as $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are given along with their IR and ^1H and ^{13}C NMR data. Although we did not manage to isolate higher nuclearity Ga(III) complexes in our first attempt, we continue working toward the synthesis of polynuclear Ga(III) complexes with salicylaldoximes.

Appendix A. Supplementary data

CCDC 729176 and 729177 contain the supplementary crystallographic data for (**1**) and (**2**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.04.039.

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