# Structural characterization of two lipophilic tris(tropolonato) gallium(III) and indium(III) complexes of radiopharmaceutical interest

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## Abstract

Tris(tropolonato)gallium(III), $GaT_3$, and tris(tropolonato)indium(III), $InT_3$, have been prepared in water from tropolone and the corresponding metal(III) nitrate salt and structurally characterized. $GaT_3$ (**1**) crystallizes in the monoclinic space group *C2/c* with $a=10.899(1)$, $b=10.282(1)$, $c=16.970(2)$ Å, $\beta=103.721(8)°$ and $Z=4$. $InT_3$ (**2**) crystallizes in the rhombohedral space group $R\bar{3}c$ with $a=10.5349(5)$, $b=10.5349(5)$, $c=32.738(2)$ Å and $Z=6$. The structures have been refined to an *R* factor of 0.027 for **1**, based on 2171 observed reflections, and to an *R* factor of 0.030 for **2**, based on 507 observed reflections. The octahedral coordination of the metal(III) ions leads to an O–M–O′ bond angle of 81.1(1)° (mean value) in **1** and 75.3(1)° in **2** and to an M–O bond length of 1.967(1) Å (mean value) in **1** and 2.134(3) Å in **2**. Structural parameters are compared to $AlT_3$ and $FeT_3$ analogues and show the inflexibility of the tropolonato anion. The structural variations observed in the parameters external to the ring are consistent with the variation of the ionic radius in this series. The five signals observed on the $^{13}C$ NMR spectra are consistent with the $C_{2v}$ symmetry of the tropolonato ligand. A downfield shift for each carbon atom is observed upon complexation.

## Introduction

Gallium and indium have isotopes that are compatible with current nuclear medical technology, and radiopharmaceuticals based on these two metal ions are in routine use for human studies [1, 2]. Only oxidation state(III) is important for gallium and indium under physiological conditions. The combination of necessary properties such as water solubility, neutral charge and lipophilicity, explains why the coordination chemistry of these elements that is relevant to their radiopharmaceutical development has remained a limited field. In recent years a variety of ligands have been investigated as potential agents for expanding the range of applications for gallium and indium radioisotopes. The bidentate chelating ligands 8-hydroxyquinoline (oxine) and 2-hydroxy-2,4,6-cycloheptatrienone (tropolone, HT) are prominent among these, since they can form neutral and lipophilic complexes and may penetrate cell membranes [3–7].

Physico-chemical data have been presented [8–15] for tris(tropolonato)metal(III) complexes, $MT_3$ (T = tropolonato anion), but structural data are limited to the tris(tropolonato)aluminium(III), $AlT_3$, [16] and to the tris(tropolonato)manganese(III), $MnT_3$, [17]. A preliminary account of the structure of $FeT_3$ has appeared [18]. No structural data have been reported for gallium(III) and indium(III) tropolonates.

In this report, the tris(tropolonato)metal(III) complexes, $[Ga(C_7H_5O_2)_3]$ (**1**) and $[In(C_7H_5O_2)_3]$ (**2**), are synthesized and spectroscopically characterized. The structures of $GaT_3$ and $InT_3$ are compared to their Group 13 congener $AlT_3$, and to $FeT_3$ because of the similarities between these four metal(III) ions.

## Experimental

### *Material and methods*

All chemicals were reagent grade and were used as received. Tropolone and metal nitrates were obtained from Aldrich. Chloroform (Prolabo) was dried over molecular sieves. Elemental analyses were performed

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by the Service Interuniversitaire de Microanalyse, ENSCT, Toulouse. Solid-state IR spectra were measured in KBr pellets on a Perkin-Elmer 1310 IR spectrophotometer. UV–Vis spectra, in solution, were recorded on a Perkin-Elmer-554 spectrophotometer. NMR spectra were recorded on a Bruker AC 250 MHz spectrometer. The preparations of the complexes are quite similar and complete details are given below. It was difficult to obtain single crystals of a suitable size for X-ray crystallography. Crystals are slightly unstable and kept in the mother liquor, but it was not necessary to mount them in glass capillaries for X-ray data collection.

### *Tris(tropolonato)gallium(III), GaT$_3$ (1)*

To a solution of tropolone (0.183 g, 1.5 mmol) in water (5 ml, 80 °C) was added an aqueous solution of gallium nitrate hydrate (99.999%) (0.128 g, 0.5 mmol, 2 ml). A white solid precipitated out immediately. After stirring (10 min), it was removed by filtration, washed with water (10 ml) and dried (0.21 g, 93%). Recrystallization of the white compound from a chloroform:hexane solution (50:15, vol.:vol.) one night at 4 °C, gave the title compound as orange–brown microcrystals (0.13 g, 66%). Crystals suitable for X-ray analysis were obtained from DMSO (67.55 mg, 12 ml, 80 °C) by slow evaporation over two weeks. Solubility (mmol$\times$l$^{-1}$) (25 °C): water ($<0.34$), chloroform (12), DMSO (63). *Anal.* Calc. for $C_{21}H_{15}GaO_6$: C, 56.78; H, 3.35%. Found: C, 57.18; H, 3.29. IR ($\nu_{max}$ (cm$^{-1}$)): $\nu$(C–C) 1597(s); $\nu$(C–O)+$\nu$(C–C) 1517(s); $\nu$(C–C) 1430(s); $\delta$(C–H) 1419(s, br); $\nu$(C–O) 1360(s, br), 1307(w); $\delta$(C–H) 1269(m), 1264(m), 1230(s); $\nu$(C–C) and $\nu$(C–H) 1086(m), 1029(w), 1011(w), 980(m), 938(m), 887(s); $\delta$(C–H) 775(m), 748(s), 720(s). UV–Vis ($CDCl_3$, $10^{-5}$ M, $\lambda_{max}$ (nm) $\epsilon$ (l cm$^{-1}$ mol$^{-1}$)): 384 (13 800), 374 (15 450), 366 (14 475), 328 (25 650), 320 (25 500). NMR ($CDCl_3$, $\delta$s/TMS, [carbon atom no.]). $^{13}$C NMR (62.9 MHz): 176.47 [1] and [1′], 139.64 [2] and [2′], 127.76 [4], 126.11 [3] and [3′]. $^1$H NMR (250 MHz): 7.07, 7.08, 7.10, 7.105, 7.11, 7.12, 7.125, 7.13, 7.14, 7.15 (H[4], $J$(H[4]–H[3], H[3′]) = 8.25, $J$(H[4]–H[2], H[2′]) = 2.15 Hz), 7.48, 7.53, 7.55, 7.56, 7.565, 7.595, 7.60, 7.61 (four protons: H[2], H[2′], H[3], H[3′]).

### *Tris(tropolonato)indium(III), InT$_3$ (2)*

The procedure was the same as for **1**. Tropolone (0.183 g, 1.5 mmol) and $In(NO_3)_3\cdot 5H_2O$ (99.99%) (0.195 g, 0.5 mmol) gave 0.22 g of white product (92%). Orange–brown crystals were obtained from a chloroform:hexane solution (70:15, vol./vol.) after 3 days at 4 °C, filtration and drying. Crystals for X-ray data collection were obtained from DMSO (62 mg, 15 ml, 80 °C) by slow evaporation over 3 weeks. Solubility (mmol l$^{-1}$) (25 °C): water ($<0.84$), chloroform (12), DMSO (65). *Anal.* Calc. for $C_{21}H_{15}InO_6$: C, 51.75; H, 3.16%. Found: C, 51.59; H, 3.03. IR ($\nu_{max}$ (cm$^{-1}$)): $\nu$(C–C) 1600(s); $\nu$(C–O) and $\nu$(C–C) 1520(s, br); $\nu$(C–C) 1430(m, br); $\nu$(C–O) 1350(s, br); $\delta$(C–H) 1275(m), 1245(m), 1220(s, br); $\nu$(C–C) and $\nu$(C–H) 1089(m), 1027(w), 987(m), 961(m), 886(s); $\delta$(C–H) 765(m), 730(br), 715(s). UV–Vis ($CDCl_3$, $10^{-5}$ M, $\lambda_{max}$ (nm) ($\epsilon$ (l cm$^{-1}$ mol$^{-1}$)): 384 (6300), 374 (8700), 366 (8625), 330 (14 250), 322 (14 400). NMR ($CDCl_3$, $\delta$s/TMS [carbon atom no.]). $^{13}$C NMR (62.9 MHz): 177.12 [1] and [1′], 138.95 [2] and [2′], 127.86 [4], 127.40 [3] and [3′]. $^1$H NMR (250 MHz): 7.06, 7.065, 7.07, 7.095, 7.10, 7.11, 7.12, 7.135, 7.14, (H[4], $J$(H[4]–H[3], H[3′]) = 9.28, $J$(H [4]–H[2], H[2′]) = 0.85 Hz), 7.47, 7.505, 7.51, 7.515, 7.55, 7.605, 7.61, 7.65, 7.655 (four protons: H[2], H[2′], H[3], H[3′]).

### *Tropolone*

UV–Vis ($CDCl_3$, $10^{-5}$ M, $\lambda_{max}$ (nm) ($\epsilon$ (l cm$^{-1}$ mol$^{-1}$)): 304 (7500), 318 (8550), 336 (6600), 350 (7350), 368 (5550). NMR ($CDCl_3$, $\delta$s/TMS [carbon atom no.]). $^{13}$C NMR (62.9 MHz): 171.86 [1] and [1′], 137.77 [2] and [2′], 126.35 [4], 123.96 [3] and [3′]. $^1$H NMR (250 MHz): 6.985, 6.995, 7.00, 7.02, 7.025, 7.03, 7.04, 7.055, 7.06, 7.07 (H[4], $J$(H[4]–H[3], H[3′]) = 8.52, $J$(H[4]–H[2], H[2′]) = 2.03 Hz); 7.25, 7.30, 7.31, 7.345, 7.35, 7.39, 7.49, 7.43 (five protons: H[1], H[2], H[2′], H[3], H[3′], $J$(H[2]–H[3]) = 11.02 Hz).

### *X-ray crystallographic analyses*

Intensities were measured at room temperature on a STOE-STADI-4 diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Experimental details of data collection and reduction are given in Table 1 along with the crystal parameters. Lattice parameters were determined from 114 reflections with $2\theta = 25$–$32°$ for **1** and from 213 reflections with $2\theta = 25$–$34°$ for **2** using the scan mode $\omega$: $\theta = 1{:}1$. Intensities were collected in the range $5 < 2\theta < 60°$, *hkl*: $-15$ to 15, $-12$ to 14, $-20$ to 23 for **1** and in the range $5 < 2\theta < 50°$, *hkl*: $-10$ to 10, $-10$ to 12, $-38$ to 38 for **2**. Systematic extinctions (see 'Supplementary material') revealed the space groups $C2/c$ or $Cc$ for compound **1** and $R\bar{3}c$ or $R3c$ for compound **2**. The refinement in the higher symmetric space groups was successful and confirmed the existence of centres of symmetry for both compounds. At this point it became apparent that the gallium complex was not isostructural with the indium analogue. The intensities of three standard reflections measured every hour showed no significant variations throughout data collections. The data were corrected for Lorentz and polarization effects. Numerical absorption correction was applied for **1** (transmission factors: 0.467–0.841). The structures were solved by direct methods (SHELXS-86) [19] and refined

TABLE 1. Crystallographic data for **1** and **2**

| Parameter | **1** | **2** |
|---|---|---|
| Formula | $GaC_{21}H_{15}O_6$ | $InC_{21}H_{15}O_6$ |
| Molecular mass | 433.05 | 478.15 |
| Crystal shape | plate-like | plate-like |
| Crystal dimensions (mm) | 0.6×0.6×0.12 | 0.4×0.4×0.1 |
| Crystal system | monoclinic | rhombohedral |
| Space group | *C*2/*c* | *R*$\bar{3}$*c* |
| *a* (Å) | 10.899(1) | 10.5349(5) |
| *b* (Å) | 10.282(1) | 10.5349(5) |
| *c* (Å) | 16.970(2) | 32.738(2) |
| $\beta$ (°) | 103.721(8) | 90 |
| *V* (Å$^3$) | 1847.43 | 3146.62 |
| *Z* | 4 | 6 |
| $D_{calc}$ (cm$^{-3}$) | 1.56 | 1.51 |
| *F*(000) | 880 | 1428 |
| $\mu$ (cm$^{-1}$) | 14.52 | 10.51 |
| Scan range, 2$\theta$ (°) | 5–60 | 5–50 |
| No. reflections measured | 6915 | 1489 |
| Unique | 2704 | 625 |
| Observed ($F_o > 3\sigma(F_o)$) | 2171 | 507 |
| No. parameters | 151 | 55 |
| Max. and min. $\Delta\rho$ (e Å$^{-3}$) | 0.26–0.35 | 0.38–0.35 |
| $R = \Sigma([F_o] - [F_c])/\Sigma[F_o]$ | 0.027 | 0.030 |
| $R_w = [(\Sigma w[F_o] - [F_c])^2/\Sigma w[F_o]^2]^{1/2}$ | 0.022 | 0.023 |

TABLE 2. Final atomic coordinates and isotropic thermal parameters with e.s.d.s in parentheses for **1** and **2**

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Complex **1** | | | | |
| Ga1 | 0.00000 | 0.14936(2) | 0.75000 | 0.0327(1) |
| O1 | −0.1184(1) | 0.0047(1) | 0.7164(1) | 0.0389(5) |
| O2 | −0.1230(1) | 0.2782(1) | 0.6931(1) | 0.0367(5) |
| O3 | 0.0577(1) | 0.1642(1) | 0.6488(1) | 0.0403(5) |
| C1 | −0.1135(1) | 0.3054(1) | 0.6204(1) | 0.0332(7) |
| C2 | −0.1996(2) | 0.3927(2) | 0.5734(1) | 0.0421(8) |
| C3 | −0.2113(2) | 0.4347(2) | 0.4940(1) | 0.0498(9) |
| C4 | −0.1398(2) | 0.4061(2) | 0.4398(1) | 0.0557(10) |
| C5 | −0.0363(2) | 0.3261(2) | 0.4524(1) | 0.0569(11) |
| C6 | 0.0209(2) | 0.2545(2) | 0.5204(1) | 0.0493(10) |
| C7 | −0.0093(1) | 0.2409(1) | 0.5954(1) | 0.0353(7) |
| C1′ | −0.0687(1) | −0.1090(1) | 0.7322(1) | 0.0309(7) |
| C2′ | −0.1459(2) | −0.2188(2) | 0.7169(1) | 0.0374(8) |
| C3′ | −0.1166(2) | −0.3501(2) | 0.7261(1) | 0.0426(8) |
| C4′ | 0.00000 | −0.4089(2) | 0.75000 | 0.0473(13) |
| Complex **2** | | | | |
| In | 0.00000 | 0.00000 | 0.25000 | 0.0325(4) |
| O1 | 0.1909(4) | 0.0609(4) | 0.2140(1) | 0.041(2) |
| C1 | 0.2887(6) | 0.0339(5) | 0.2298(1) | 0.036(2) |
| C2 | 0.4160(7) | 0.0710(7) | 0.2076(2) | 0.052(3) |
| C3 | 0.5352(9) | 0.0574(9) | 0.2162(2) | 0.0743(10) |
| C4 | 0.5666(9) | 0.0000 | 0.2500 | 0.090(10) |

with STRUXI [20]. All hydrogen atoms were observed on a difference-Fourier map and their positions were refined with fixed isotropic thermal parameters ($\mu_{iso} = 0.05$ Å$^2$). Maximum shift/e.s.d. in final cycle were $< 0.06$ for **1** and $< 0.005$ for **2**. The extinction corrections used were $7.7 \times 10^{-4}$ for **1** and $1.8 \times 10^{-4}$ for **2**. No significant feature appeared in the final difference-Fourier maps. Atomic scattering factors were taken from ref. 21. Diagrams were drawn with SHELXTL-Plus [22]. Final atomic coordinates and isotropic thermal parameters ($U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$) are given in Table 2. Selected interatomic distances and angles are listed in Tables 3 and 4. See also 'Supplementary material'.

## Results and discussion

The compounds **1** and **2** have been prepared in a manner different from that reported previously [10a]. The Ga and In complexes of tropolone can be prepared from aqueous solution of the metal nitrate salts with a very good yield.

The complexes are soluble in chloroform ($10^{-2}$ M) and poorly soluble in water ($10^{-4}$ M). *In vitro* partition ratios of the gallium and indium tropolonates, correlated with *in vivo* organ distribution in the rat, have been determined previously by Hendershott *et al.* [5]. These studies showed that these metal complexes are highly lipid soluble.

TABLE 3. Bond lengths (Å) and bond angles (°) with e.s.d.s for **1**

| | | | |
|---|---|---|---|
| Ga(1)–O(1) | 1.963(1) | | |
| Ga(1)–O(2) | 1.967(1) | | |
| Ga(1)–O(3) | 1.970(1) | | |
| O(1)–C(1′) | 1.288(2) | C(1)–O(2)–Ga(1) | 114.5(1) |
| O(2)–C(1) | 1.293(2) | C(7)–O(3)–Ga(1) | 114.6(1) |
| O(3)–C(7) | 1.289(2) | O(2)–C(1)–C(2) | 119.1(1) |
| C(1)–C(2) | 1.402(2) | O(2)–C(1)–C(7) | 114.9(1) |
| C(2)–C(3) | 1.392(3) | C(2)–C(1)–C(7) | 126.0(2) |
| C(3)–C(4) | 1.371(3) | O(3)–C(7)–C(6) | 119.1(2) |
| C(4)–C(5) | 1.371(3) | O(3)–C(7)–C(1) | 115.1(1) |
| C(5)–C(6) | 1.386(3) | C(1)–C(2)–C(3) | 130.1(2) |
| C(6)–C(7) | 1.395(3) | C(2)–C(3)–C(4) | 130.3(2) |
| C(7)–C(1) | 1.463(2) | C(3)–C(4)–C(5) | 127.0(2) |
| O(1)–C(1′) | 1.288(2) | C(4)–C(5)–C(6) | 129.7(2) |
| C(1′)–C(2′) | 1.395(2) | C(5)–C(6)–C(7) | 131.1(2) |
| C(2′)–C(3′) | 1.388(2) | C(1)–C(7)–C(6) | 125.8(1) |
| C(3′)–C(4′) | 1.379(2) | C(1′)–O(1)–Ga(1) | 114.3(1) |
| | | O(1)–C(1′)–C(2′) | 119.4(1) |
| | | O(1)–C(1′)–C(1′a) | 114.9(1) |
| O(1)–Ga(1)–O(1a) | 81.4(1) | C(2′)–C(1′)–C(1′a) | 125.8(1) |
| O(1)–Ga(1)–O(2) | 92.5(1) | C(1′)–C(2′)–C(3′) | 130.9(2) |
| O(1)–Ga(1)–O(2a) | 167.7(1) | C(4′)–C(3′)–C(2′) | 129.2(2) |
| O(1)–Ga(1)–O(3) | 97.5(1) | C(3′)–C(4′)–C(3′a) | 127.9(2) |
| O(1)–Ga(1)–O(3a) | 89.3(1) | | |
| O(2)–Ga(1)–O(2a) | 95.3(1) | | |
| O(2)–Ga(1)–O(3) | 80.8(1) | | |
| O(2)–Ga(1)–O(3a) | 93.1(1) | | |
| O(3)–Ga(1)–O(3a) | 171.1(1) | | |

TABLE 4. Bond lengths (Å) and bond angles (°) with e.s.d.s for **2**

| | |
|---|---|
| In(1)–O(1) | 2.134(3) |
| O(1)–C(1) | 1.304(8) |
| C(1)–C(1′) | 1.464(6) |
| C(1)–C(2) | 1.398(8) |
| C(2)–C(3) | 1.362(14) |
| C(3)–C(4) | 1.378(10) |
| O(1)–In(1)–O(1c) | 75.3(1) |
| O(1)–In(1)–O(1a) | 92.4(1) |
| O(1)–In(1)–O(1e) | 103.2(1) |
| O(1)–In(1)–O(1d) | 160.4(2) |
| In(1)–O(1)–C(1) | 116.4(3) |
| O(1)–C(1)–C(2) | 119.1(4) |
| C(1)–C(2)–C(3) | 132.1(6) |
| C(2)–C(3)–C(4) | 130.4(7) |
| C(3)–C(4)–C(3′) | 125.2(7) |

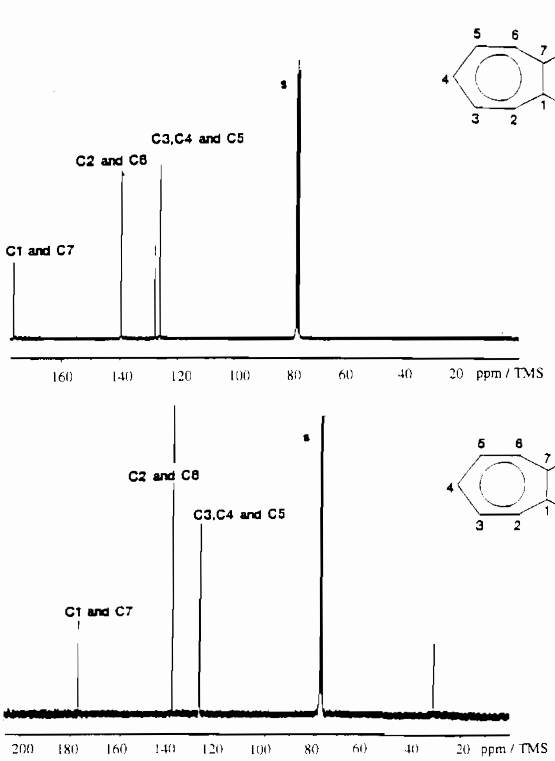

Fig. 1. $^{13}C$ NMR spectra in $CDCl_3$ for **1** and **2**.

The IR spectral pattern (1613–713 $cm^{-1}$), which is characteristic of tropolone [15], is preserved in the complexes, with a general bathochromic shift upon complexation (see 'Experimental'). The observed bands are in agreement with IR spectral studies reported [11] also recently [15] for $GaT_3$.

The $^{13}C$ NMR spectra of **1** and **2** exhibit five signals due to the $C_{2v}$ symmetry of the seven carbon atom ring (Fig. 1). Chemical shifts for **1**, **2** and HT are given in 'Experimental'. A downfield shift is observed for each carbon atom, upon complexation, with the strongest effect on [1] (and [1′]). These observed chemical shifts are comparable to those reported for the galliumdimethyltropolonate complex [23]. The typical and intricate ABB′CC′M pattern, which is observed in the $^1H$ NMR spectrum of HT, at room temperature and in $CDCl_3$, persists for **1** and **2** in the form of a BB′CC′M system (Fig. 2). The pattern is composed of two distinct multiplets. The first one is a triplet (H4) centred at 7.03 ppm for HT, and at 7.11 and 7.10 ppm for **1** and **2**, respectively. The second multiplet is centred at 7.35 ppm for HT (H1, H2, H2′, H3, H3′), and at 7.59 and 7.55 ppm for **1** and **2**, respectively (H2, H2′, H3, H3′). These results show a slight downfield shift for each multiplet upon complexation.

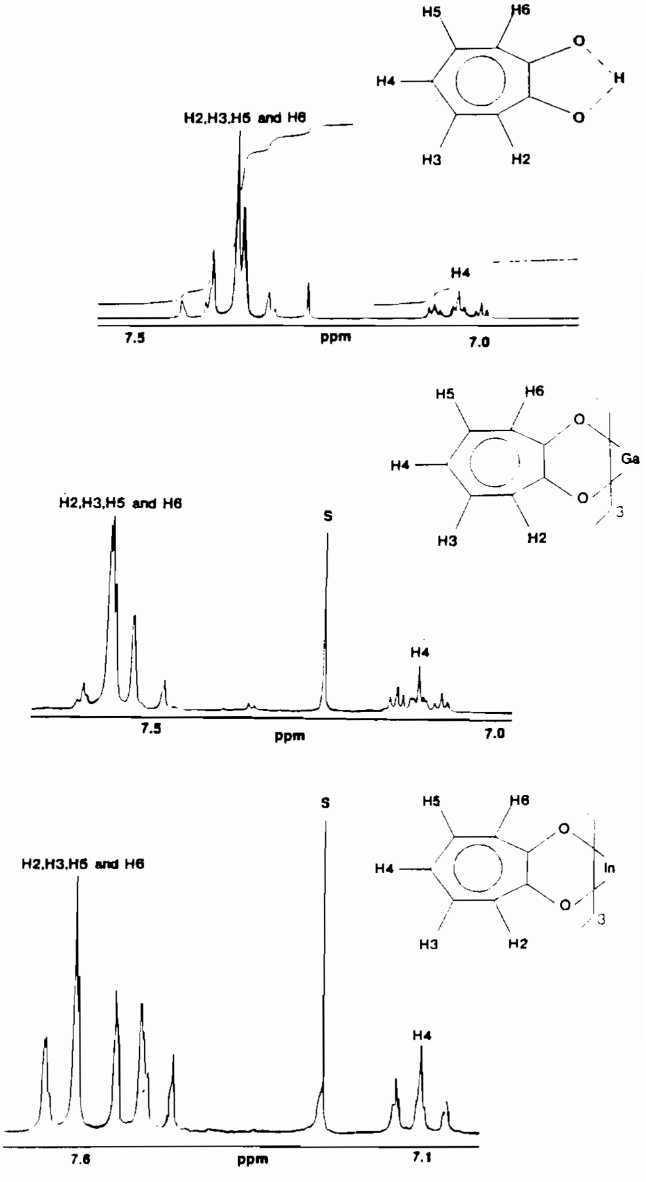

Fig. 2. $^1H$ NMR spectra in $CDCl_3$ for **1** and **2** and for tropolone.

The crystal structures of $Ga(T_3)$ (**1**) and $In(T_3)$ (**2**) have been solved. **1** and **2** are not isomorphous. The gallium complex is isomorphous with tris(tropolonato)aluminium(III) (**3**) [16], and the indium(III) complex appears to be isomorphous with the iron(III) analogue, **4** [18]. Drawings of single molecules of **1** and **2** are given, along with appropriate atom numbering schemes, in Figs. 3 and 4, respectively. A more complete picture of $InT_3$ is accessible by examination of the stereoview (Fig. 5). There is no relationship between the two structures in the sense of super-group → sub-group.

The crystal structure of **1** consists of neutral $Ga(T_3)$ units. The twofold symmetry causes the asymmetric unit to contain one-half of a metal ion, and one and a half of the ligand. The octahedral coordination of gallium by oxygens from three tropolonate anions is approximately octahedral, but deviates from the ideal configuration. The compression is seen on the O(1)–Ga–O(1a) and O(2)–Ga–O(3) angles involving oxygen atoms from the same ligand, which are 81.4 (1) and 80.8 (1)°, respectively. This can be a consequence of the dimensions of the rigid seven-ring tropolonate ligand. The exocyclic O(1)–Ga–O(3) (97.5 (1)°) and O(2)–Ga–O(2a) (95.3 (1)°) angles are both greater than 90°, as are the exocyclic O(1)–Ga–O(2) (92.5 (1)°) and O(2)–Ga–O(3a) (93.1 (1)°) angles. This two-fold axis forces equality of the two Ga–O(1) distances, but allows dissimilarity of Ga–O(2) and Ga–O(3) distances. The average Ga–O distance is 1.967 Å, while individual values are in the range 1963(1)–1.970(1) Å and are not significantly different. This mean distance is within the range of values found in comparable gallium complexes with 3-hydroxy-4-pyridinonate or hydroxamate as ligands [24, 25]. There is no significant difference between O(2)–C(1) and O(3)–C(7) bond lengths, showing the strong delocalization of the ligand (from initial distinct keto and hydroxy functions) upon complexation. The ligand is planar within experimental error (see 'Supplementary material'), Ga being displaced 0.13 Å maximum from this plane.

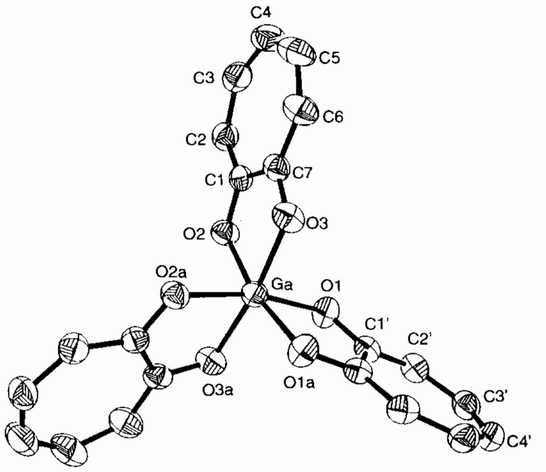

Fig. 3. Perspective view of the $Ga(T_3)$ molecule (**1**).

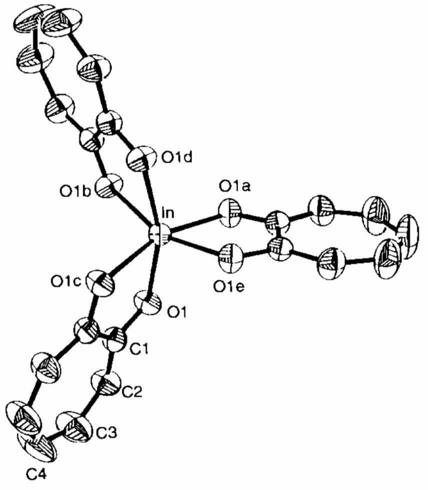

Fig. 4. Perspective view of the $In(T_3)$ molecule (**2**).

Complex **2** presents a comparable molecular structure but with a higher symmetry. The indium atom is on the 32 position and this forces 32 symmetry on the complex as a whole. The asymmetric unit consists of one-sixth of a metal ion and one-half of the ligand. The result is that there is only one independent In–O(1) bond length (2.134(3) Å), which is within the range of values found in comparable indium complexes [24, 25]. The O(1)–C(1) bond length of 1.304(8) Å is slightly longer than in **1**. There is a stronger compression of the $In(T_3)$ units from $O_h$ down the three-fold axis, leading to an intraring O(1)–In–O(1c) angle of 75.3(1)° compared with the average value of 81.1(1)° for the Ga analogue. The exocyclic O(1)–In–O(1) angles are also smaller than in the Ga analogue. This 32 symmetry imposed by the special crystallographic position at the metal ion (32) leads to a 50/50 mixture of $\Lambda$ and $\Delta$ molecules in the crystal.

Some geometric parameters of the four tris(tropolonato)metal(III) complexes, $AlT_3$, $GaT_3$, $InT_3$ and $FeT_3$ are compared in Table 5. The M–O bond length increases, and the O–M–O′ angle decreases as the ionic radius of the metal(III) ion increases. For $FeT_3$, the O…O′ distance value is intermediate between those of $AlT_3$ and $GaT_3$ and the C1–C1′ bond length is not significantly different from those of $GaT_3$ and $InT_3$. In **1** the dihedral angle between O(1) O(2) O(3a) and O(1a) O(2a) O(3) is 2.4° and the twist angles ($\phi_{11a}$, $\phi_{23}$, $\phi_{2a3a}$) are not equivalent with an average value of 46.7°. This average twist angle value is comparable to that observed in $AlT_3$ having the same crystallographic symmetry and lower than the 60° value for an idealized trigonal antiprism as in **2** or in $FeT_3$. There is no averaging of the C–C bonds in the tropolonato ligand, which are similar to those observed in tropolone, HT

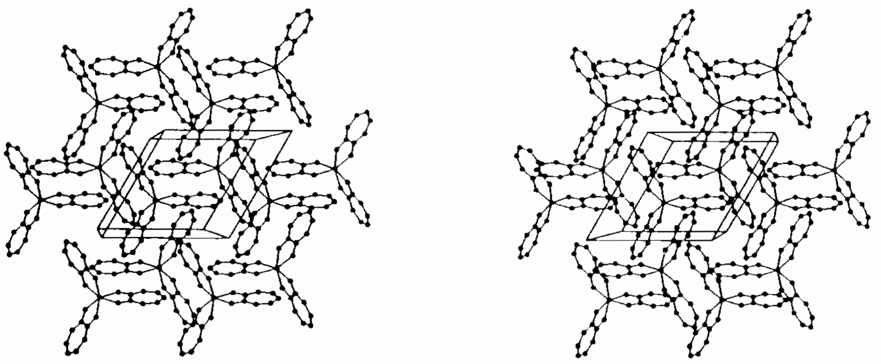

Fig. 5. Stereoview along *c* of the unit cell of In(T$_3$) (**2**).

TABLE 5. Comparison of geometric parameters[a] in tristropolonatometal(III) complexes

| Compound | Ionic radius[b] | O–M–O′ | O...O′ | M–O | O–C1 | C1–C1′ | C1–C2 | C2–C3 | C3–C4 | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| HT[c] | | | | | 1.261(3)<br>1.333(3) | 1.454(4) | 1.410(4)<br>1.379(4) | 1.373(4)<br>1.393(4) | 1.410(3)<br>1.341(4) | 27 |
| AlT$_3$[d] | 0.68 | 82.6(4) | 2.490(6) | 1.888(2) | 1.291(1) | 1.450(1) | 1.397(1) | 1.384(2) | 1.371(5) | 16 |
| GaT$_3$ | 0.76 | 81.1(1)[d] | 2.558(2) | 1.967[d](1) | 1.290[d](2) | 1.463(2) | 1.395(3)<br>1.402(2) | 1.386(3)<br>1.392(3) | 1.371(3)<br>1.371(3) | this work |
| InT$_3$ | 0.94 | 75.3(1) | 2.607(4) | 2.134(3) | 1.304(8) | 1.464(6) | 1.398(8) | 1.362(14) | 1.378(10) | this work |
| FeT$_3$ | 0.79 | 77.8(1) | 2.522(4) | 2.008(3) | 1.294(5) | 1.463(7) | 1.397(2) | 1.385(7) | 1.379(7) | 18 |

[a] Angles (°) and distances (Å) with estimated errors. [b] Ref. 26, coordination number 6. [c] Tropolone. [d] Mean values.

[27] (1.454–1.375 Å). The C(1)–C(1′) length of 1.462 Å is significantly greater than other bonds in the ring, not included in the $\pi$-electron delocalization. The C1–C2 distance is the longest of the three other types of C–C distances. A continuous decrease in bond length (C1–C2 > C2–C3 > C3–C4) is observed, except in InT$_3$, but for these lengths e.s.d. values are large. Examination of all distances in these four complexes shows that the variations in the tropolonato ligand distances are very small. Geometric variations are larger in the structural parameters external to the ring. These studies show that, for the same chelating ligand, the tropolonato anion, structural parameters of the iron(III) analogue are close either to the gallium(III) analogue or to the indium(III) analogue. These examples illustrate the similarities between the coordination chemistry of the Ga$^{3+}$, In$^{3+}$ and Fe$^{3+}$ metal ions. These similarities are manifested *in vivo* by the binding of all three ions to the serum protein transferrin normally used for ion transport.

## Supplementary material

Lists of systematic extinctions, hydrogen atom parameters, anisotropic thermal parameters, observed and calculated structure factors for **1** and **2**, least-squares planes and dihedral angles and twist angles for **1**, and a stereoview of **1** are available from author F.N. on request.

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