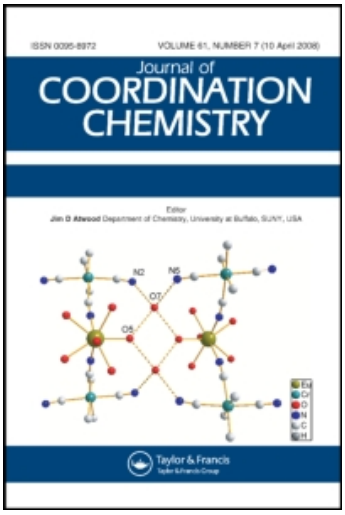


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Aluminum(III), gallium(III), and indium(III) 4-hydroxyacridinato complexes

Iolinda Aiello[a]; Daniela Aiello[a]; Mauro Ghedini[a]
[a] Centre of Excellence CEMIF.CAL; LASCAMM, CR-INSTM Reference Centre of Italian Interuniversity Consortium on Materials Science and Technology, Department of Chemistry, University of Calabria, Italy

To cite this Article Aiello, Iolinda , Aiello, Daniela and Ghedini, Mauro(2009) 'Aluminum(III), gallium(III), and indium(III) 4-hydroxyacridinato complexes', Journal of Coordination Chemistry, 62: 20, 3351 — 3365
To link to this Article: DOI: 10.1080/00958970903071625
URL: http://dx.doi.org/10.1080/00958970903071625

Journal of Coordination Chemistry
Vol. 62, No. 20, 20 October 2009, 3351–3365

Taylor & Francis
Taylor & Francis Group

Aluminum(III), gallium(III), and indium(III) 4-hydroxyacridinato complexes

IOLINDA AIELLO*, DANIELA AIELLO and MAURO GHEDINI

Centre of Excellence CEMIF.CAL; LASCAMM, CR-INSTM Reference Centre of Italian Interuniversity Consortium on Materials Science and Technology, Department of Chemistry, University of Calabria, I-87036 Arcavacata di Rende (CS), Italy

(*Received 4 December 2008; in final form 10 April 2009*)

4-Hydroxyacridine (HAcr) is an O,N-chelating ligand whose coordination chemistry toward group 13 M(III) ions has received little attention. The molecular structure of HAcr consists of a 2,3-disubstituted-8-hydroxyquinoline; thus, in order to compare 8-hydroxyquinoline (HQ), 2-methyl-8-hydroxyquinoline (HMeQ′), and 2,3-disubstituted-8-hydroxyquinoline (HAcr) for steric and/or electronic influence, HAcr chelating ability toward the Al(III), Ga(III), and In(III) triad has been investigated. Irrespective of the nature of M(III), only complexes containing two equivalents of deprotonated HAcr are obtained. This article describes the synthesis and characterization of different series of bis-chelated pentacoordinated $(Acr)_2MY$ (M = Al, Ga, In; Y = Cl, Br, I, NCS, N_3) or $(Acr)_2MZ$ (M = Ga or In; HZ = C_6H_5OH, $C_6H_{13}OC_6H_4OH$, C_6H_5COOH, or $C_6H_{13}OC_6H_4COOH$) six-coordinate neutral $(Acr)_2In(acac)$ (H(acac) = acetylacetone), or ionic $[(Acr)_2In(N,N)][CF_3SO_3]$ (N,N = 2,2′-bipyridine or 1,10-phenanthroline) complexes. These results significantly contribute to elucidating the complexation capability of HAcr.

Keywords: 4-Hydroxyacridine complexes; Group 13 elements; N,O ligands

1. Introduction

M(III) ions (M = Al, Ga, or In), reacting with 8-hydroxyquinoline (HQ; in figure 1), form hexacoordinate MQ_3 [1] complexes, which have been extensively investigated for their luminescent properties, leading to patents for a new generation of multilayer, not fully inorganic, electroluminescent light emitting devices [2]. These devices, currently referred to as Organic Light Emitting Devices (OLEDs), contain a molecular material (i.e. AlQ_3) which acts both as electron transport and emitting layer [3].

The admission of AlQ_3 into the field of advanced materials further stimulated investigations on AlQ_3-like compounds. To this end, the 2-methyl-8-hydroxyquinoline (HMeQ′; in figure 1) was considered and either tris-chelated hexacoordinate $M(MeQ')_3$

*Corresponding author. Email: iolinda.aiello@unical.it

ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970903071625

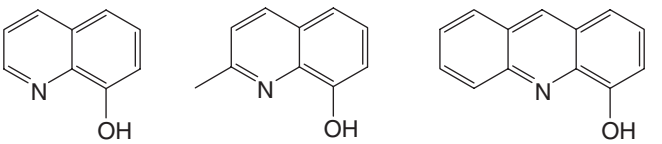


Figure 1. Molecular structure of HQ, HMeQ′, and HAcr.

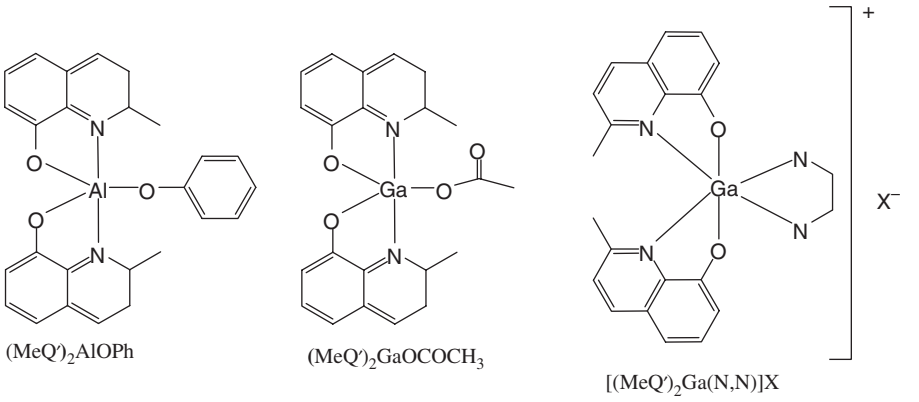


Figure 2. Molecular structure of $(MeQ')_2AlOPh$, $(MeQ')_2GaOCOCH_3$, and $[(MeQ')_2Ga(N,N)]X$ complexes.

(M = Al [4], Ga [5] or In [5a, 5b]) or bis-chelated pentacoordinate $(MeQ')_2MOL$ (M = Al [6] or Ga [5c, 7]) compounds were synthesized and investigated (representative examples of which are M = Al, L = Ph, $(MeQ')_2AlOPh$ [6h] and M = Ga, L = $COCH_3$, $(MeQ')_2GaOCOCH_3$ [7a], respectively, in figure 2).

For HQ or HMeQ′ complexes, while the MQ_3 series is obtained irrespective of the molar ratio between M(III) and HQ, the products which HMeQ′ form depend on the nature of M(III). When treating Al(III) with HMeQ′, in any molar ratio and in presence of phenol or substituted phenols, $(MeQ')_2AlOL$ [6] complexes usually form (except for the synthesis of $Al(MeQ')_3$ which requires very specific reaction conditions [4]). In contrast, Ga(III) with HMeQ′ in a 1 : 3 molar ratio quantitatively forms $Ga(MeQ')_3$, whereas in 1 : 2 molar ratio, although in presence of an excess of the pertinent carboxylic acid or the phenol, both hexacoordinate $Ga(MeQ')_3$ and pentacoordinate $(MeQ')_2GaOL$ [5c, 7] complexes form. Finally, In(III) and HMeQ′ exclusively forms $In(MeQ')_3$ [5a, 5b].

The coordination chemistry of HQ or HMeQ′ with the Al(III)–In(III) triad is well documented and formation of hexacoordinate MQ_3 or $M(MeQ')_3$ depends on the right balance between O,N steric hindrance and the M(III) ionic radius (Al(III), 51 pm; Ga(III), 62 pm; In(III), 81 pm) [8]. Indeed, in mild reaction conditions, the smaller Al(III) with the comparatively bulkier HMeQ′ bearing the Me group in position 2 of the quinoline skeleton gives only the bis-chelated complex of general formula $(MeQ')_2AlOL$. In contrast, with the intermediate sized Ga(III), both the tris-chelated $Ga(MeQ')_3$ and the bis-chelated $(MeQ')_2GaOL$ coordination compounds are obtained, while with the larger In(III) only $In(MeQ')_3$ is formed. Recently, $[(MeQ')_2Ga(N,N)]X$

compounds have also been synthesized and structurally characterized (N,N = 2,2′-bipyridine or 1,10-phenanthroline; $X^- = NO_3^-$ or PF_6^- [9] in figure 2).

4-Hydroxyacridine (HAcr, in figure 1) is an O,N-chelating ligand with steric hindrance similar to that of a 2,3-disubstituted-8-hydroxyquinoline. Remarkably, literature data concerning HAcr coordination chemistry with group 13 M(III) ions are nonexistent. Thus, in order to compare how O,N steric hindrance determines both the stoichiometry and the nature of the coordination polyhedron of the M(III) complexes along the homologous series of HQ, HMeQ′, and HAcr, HAcr chelation toward the Al(III)–In(III) triad was investigated.

This article describes the synthesis and characterization of bis-chelated pentacoordinate $(Acr)_2MY$ (M = Al, Ga, In; Y = Cl, Br, I, NCS, N_3) or $(Acr)_2MZ$ (M = Ga or In; HZ = C_6H_5OH, $C_6H_{13}OC_6H_4OH$, C_6H_5COOH, or $C_6H_{13}OC_6H_4COOH$), hexacoordinate neutral $(Acr)_2In(acac)$ (H(acac) = acetylacetone), or ionic $[(Acr)_2In(N,N)][CF_3SO_3]$ (N,N = 2,2′-bipyridine or 1,10-phenanthroline) complexes.

2. Experimental

2.1. *General considerations*

Commercially available chemicals were used without purification. ^{1}H NMR spectra were recorded on a Bruker WM-300 at room temperature with Me_4Si as internal standard. IR spectra as KBr pellets were recorded on a Perkin-Elmer 2000 FT-IR. Elemental analyses were performed with a CHNS/O Perkin-Elmer 2400 analyzer. The melting points were determined with a microscope (Zeiss Axioscop) equipped with a Linkam CO 600 heating stage. Absorption spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer.

2.2. *Preparation of $(Acr)_2MX$ (1, 2, and 3a)*

Complexes **1**–**3** were prepared by a similar procedure using $AlCl_3$, $GaNO_3 \cdot xH_2O$, and $InCl_3$, respectively. The detailed procedure for preparation of **1** is given in Section 2.2.1.

2.2.1. $(Acr)_2AlOH$ (1). A solution of $AlCl_3$ (50 mg, 0.375 mmol) in water : ethanol (5 : 5 mL) was added to a stirred ethanolic solution (15 mL) of HAcr (146 mg, 0.75 mmol) containing sodium hydroxide (30 mg, 0.75 mmol). The resulting mixture was continuously stirred for 5 h at reflux and for 16 h at room temperature. The obtained suspension was collected by filtration and the resultant solution was reduced. Diethyl ether was then added to give a bright orange precipitate of **1** that was collected by filtration. Yield: 130 mg (80%): m.p. = 205°C. ^{1}H NMR (CD_3OD): δ 9.89 (s, 2H, $H^{4,4\prime}$), 8.58 (d, 2H, J = 8.95 Hz, $H^{8,8\prime}$), 8.48 (d, 2H, J = 8.51 Hz, $H^{5,5\prime}$), 8.28 (t, 2H, J = 7.77 Hz, $H^{7,7\prime}$), 7.95 (t, 2H, J = 6.38 Hz, $H^{6,6\prime}$), 7.90 (d, 2H, J = 7.78 Hz, $H^{3,3\prime}$), 7.78 (t, 2H, J = 7.99 Hz, $H^{2,2\prime}$), 7.59 (d, 2H, J = 7.48 Hz, $H^{1,1\prime}$) ppm. IR (KBr): ν 2826 (br s, OH), 1631 (m), 1516 (m), 1468 (m), 1143 (m), 1075 (m), and 729 (s) cm^{-1}. UV-Vis (CH_3OH): λ_{max} = 440, 360, 343, and 270 nm. Anal. Calcd for $C_{26}H_{17}N_2O_3Al$ (%): C, 72.22; H, 3.96; N, 6.48. Found (%): C, 72.0; H, 3.92; N, 6.43.

2.2.2. $(Acr)_2GaNO_3$ (2). In this case, $Ga(NO_3)_3 \cdot xH_2O$ (50 mg, 0.195 mmol) and HAcr (76 mg, 0.391 mmol) were used. The resulting precipitate was filtered and repeatedly washed with water and ethanol. A bright orange solid was obtained. Yield: 86 mg (85%): m.p. >300°C. IR (KBr): ν 3055 (m), 1625 (m), 1523 (m), 1340–1281 (s, NO), 1142 (m), 1085 (m), and 760 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 451$, 363, 345, and 276 nm. Anal. Calcd for $C_{26}H_{16}N_3O_5Ga$ (%): C, 60.04; H, 3.10; N, 8.08. Found (%): C, 59.68; H, 2.93; N, 8.13. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.2.3. $(Acr)_2InCl$ (3a). For **3a**, $InCl_3$ (50 mg, 0.226 mmol) and HAcr (88 mg, 0.452 mmol) were used. The resulting precipitate was filtered, repeatedly washed with water and ethanol giving a red solid. Yield: 109 mg (90%): m.p. >300°C. IR (KBr): ν 3052 (m), 1624 (w), 1519 (m), 1462 (m), 1363 (w), 1146 (w), 1080 (w), 766 (m), and 734 (m) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 466$, 365, 348, and 280 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2InCl$ (%): C, 57.97; H, 2.99; N, 5.20. Found (%): C, 58.20; H, 3.10; N, 5.20. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.3. *Preparation of $(Acr)_2AlY$ (1a–1e)*

2.3.1. $(Acr)_2AlCl$ (1a). A solution of LiCl (49 mg, 1.16 mmol) in water (6 mL) was added in a molar ratio of 10 : 1 to a stirred water solution (5 mL) of **1** (50 mg, 0.116 mmol) at room temperature. The solution was stirred for 5 days and the resulting brown precipitate was collected by filtration and purified by washing with water, ethanol, and diethyl ether. Yield: 28 mg (55%): m.p. >300°C. IR (KBr): ν 3056 (m), 1612 (m), 1519 (m), 1464 (m), 1337 (m), 1147 (m), 1084 (m), and 764 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 387$, 357, 340, and 257 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2AlCl$ (%): C, 69.26; H, 3.58; N, 6.21. Found (%): C, 69.00; H, 3.20; N, 6.11. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.3.2. $(Acr)_2AlBr$ (1b). Complex **1b** was synthesized following the procedure described for **1a** using NaBr. A brown red solid was obtained. Yield: 32 mg (57%): m.p. >300°C. IR (KBr): ν 3050 (m), 1625 (m), 1520 (m), 1467 (m), 1334 (m), 1144 (m), 1080 (m), and 764 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 389$, 360, 348, and 259 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2AlBr$ (%): C, 63.05; H, 3.26; N, 5.66. Found (%): C, 62.98; H, 3.21; N, 5.40. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.3.3. $(Acr)_2AlI$ (1c). Complex **1c** was synthesized following the procedure described for **1a** using KI. A brown solid was obtained. Yield: 37 mg (60%): m.p. >300°C. IR (KBr): ν 3051 (m), 1630 (m), 1585 (m), 1473 (m), 1419 (m), 1147 (m), 1071 (m), 870 (s), and 728 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 390$, 360, 340, and 260 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2AlI$ (%): C, 57.58; H, 2.97; N, 5.17. Found (%): C, 57.40; H, 2.80; N, 5.07. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.3.4. $(Acr)_2AlNCS$ (1d). Complex **1d** was synthesized following the procedure for **1a** using LiNCS. An orange-red solid was obtained. Yield: 30 mg (56%): m.p. > 300°C.

IR (KBr): ν 3053 (m), 2068 (CN, m), 1625 (m), 1513 (m), 1462 (m), 1378 (m), 1147 (m), 1080 (m), and 757 (m) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 384$, 364, 342, and 265 nm. Anal. Calcd for $C_{27}H_{16}N_3O_2AlS$ (%): C, 68.49; H, 3.41; N, 8.87. Found (%): C, 68.30; H, 3.18; N, 8.84. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.3.5. $(Acr)_2AlN_3$ (1e). Complex **1e** was synthesized following the procedure described for **1a** using NaN_3. A brown-orange solid was obtained. Yield: 28 mg (53%): m.p. >300°C. IR (KBr): ν 3058 (m), 2131 (N_3, m), 2053 (N_3, m), 1615 (m), 1520 (m), 1466 (m), 1334 (m), 1144 (m), 1082 (m), and 765 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 382$, 357, 340, and 257 nm. Anal. Calcd for $C_{26}H_{16}N_5O_2Al$ (%): C, 68.27; H, 3.53; N, 15.31. Found (%): C, 68.00; H, 3.42; N, 15.20. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.4. *Preparation of $(Acr)_2GaY$ (2a–2e)*

2.4.1. $(Acr)_2GaCl$ (2a). Complex **2a** was obtained as for **1a** using acetone : water (8:5 mL). A bright orange-yellow solid was obtained. Yield: 38 mg (80%) : m.p. >300°C. IR (KBr): ν 3054 (m), 1624 (m), 1522 (m), 1398 (m), 1143 (m), 1083 (m), and 757 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 450$, 362, 296, and 275 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2GaCl$ (%): C, 63.27; H, 3.27; N, 5.68. Found (%): C, 62.92; H, 3.50; N, 5.72. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.4.2. $(Acr)_2GaBr$ (2b). Complex **2b** was synthesized following the procedure described for **1a** using NaBr. An orange solid was obtained. Yield: 45 mg (87%): m.p. >300°C. IR (KBr): ν 3049 (m), 1609 (m), 1530 (m), 1462 (m), 1237 (m), 1147 (m), 1082 (m), and 734 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 450$, 361, 343, and 273 nm. Anal. Calcd. for $C_{26}H_{16}N_2O_2GaBr$ (%): C, 58.04; H, 3.00; N, 5.21. Found (%): C, 58.40; H, 2.83; N, 4.93. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.4.3. $(Acr)_2GaI$ (2c). Complex **2c** was synthesized following the procedure described for **1a** using KI. An orange-red solid was obtained. Yield: 42 mg (74%): m.p. >300°C. IR (KBr): ν 3050 (m), 1610 (m), 1528 (m), 1363 (m), 1146 (m), 1082 (m), and 745 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 456$, 361, 346, and 276 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2GaI$ (%): C, 53.38; H, 2.76; N, 4.79. Found (%): C, 53.41; H, 2.98; N, 4.55. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.4.4. $(Acr)_2GaNCS$ (2d). Complex **2d** was synthesized following the procedure described for **1a** using LiNCS. An orange-red solid was obtained. Yield: 35 mg (70%): m.p. >300°C. IR (KBr): ν 3054 (m), 2070 (CN, m), 1635 (m), 1518 (m), 1465 (m), 1388 (m), 1148 (m), 1084 (m), and 767 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 443$, 360, 345, and 272 nm. Anal. Calcd for $C_{27}H_{16}N_3O_2GaS$ (%): C, 62.82; H, 3.12; N, 8.14. Found (%): C, 62.79; H, 2.99; N, 7.93. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.4.5. $(Acr)_2GaN_3$ (2e). Complex **2e** was synthesized following the procedure described for **1a** using NaN_3. An orange-red solid was obtained. Yield: 40 mg (83%): m.p. >300°C. IR (KBr): ν 3054 (m), 2079 (N_3, m), 1624 (m), 1522 (m), 1398 (m), 1143 (m), 1083 (m), and 757 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 450$, 362, 296, and 275 nm. Anal. Calcd for $C_{26}H_{16}N_5O_2Ga$ (%): C, 62.44; H, 3.22; N, 14.0. Found (%): C, 62.11; H, 2.96; N, 13.88. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.5. *Preparation of $(Acr)_2InY$ (3b–3e)*

2.5.1. $(Acr)_2InBr$ (3b). Complex **3b** was obtained in the same way as **1a** using NaBr and water : acetone (5 : 8 mL). An orange-red solid was obtained. Yield: 35 mg (64%): m.p. >300°C. IR (KBr): ν 3052 (m), 1624 (m), 1519 (m), 1462 (m), 1283 (m), 1145 (m), 1081 (m), 740 (s), and 600 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 465$, 365, 347, and 281 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2InBr$ (%): C, 53.55; H, 2.77; N, 4.80. Found (%): C, 53.88; H, 2.77; N, 4.22. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.5.2. $(Acr)_2InI$ (3c). Complex **3c** was synthesized following the procedure described for **1a** using KI. An orange solid was obtained. Yield: 36 mg (61%): m.p. >300°C. IR (KBr): ν 3056 (m), 1623 (m), 1539 (m), 1398 (m), 1269 (m), 1146 (m), 1079 (m), 874 (s), and 733 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 471$, 365, 348, and 281 nm. Anal. Calcd for $C_{26}H_{16}N_2O_2InI$ (%): C, 49.56; H, 2.56; N, 4.45. Found (%): C, 49.86; H, 2.77; N, 4.71. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.5.3. $(Acr)_2InNCS$ (3d). Complex **3d** was synthesized following the procedure described for **1a** using LiNCS. An orange-red solid was obtained. Yield: 34 mg (66%): m.p. >300°C. IR (KBr): ν 3060 (m), 2060 (m, CN), 1624 (m), 1519 (m), 1462 (m), 1394 (m), 1145 (m), 1081 (m), and 764 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 460$, 364, 347, and 278 nm. Anal. Calcd for $C_{27}H_{16}N_3O_2InS$ (%): C, 57.77; H, 2.87; N, 7.49. Found (%): C, 57.70; H, 2.79; N, 7.30. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.5.4. $(Acr)_2InN_3$ (3e). Complex **3e** was synthesized following the procedure described for **1a** using NaN_3. An orange-red solid was obtained. Yield: 32 mg (64%): m.p. >300°C. IR (KBr): ν 3053 (m), 2066 (m, N_3), 1625 (m), 1517 (m), 1459 (m), 1337 (m), 1147 (m), 1080 (m), and 727 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 460$, 365, 347, and 282 nm. Anal. Calcd for $C_{26}H_{16}N_5O_2In$ (%): C, 57.27; H, 2.96; N, 12.84. Found (%): C, 57.10; H, 2.87; N, 12.80. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.6. *Preparation of $(Acr)_2GaZ$ (2f–2i)*

In a typical preparation, sodium hydroxide (15 mg, 0.384 mmol) was added to a solution of the suitable phenol (0.384 mmol) or carboxylic acid (0.384 mmol).

The resulting mixture was slowly added to a suspension of **2** (50 mg, 0.096 mmol) in ethanol (5 mL). The resulting mixture was refluxed for 24 h. After cooling to room temperature, the solid was filtered and washed with water, ethanol, and diethyl ether.

2.6.1. $(Acr)_2GaOC_6H_5$ (2f). Orange-red solid. Yield: 37 mg (70%): m.p. >300°C. IR (KBr): ν 3050 (m), 1624 (m), 1521 (m), 1464 (m), 1278 (m), 1148 (m), 1080 (m), 740 (s), and 619 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 443$, 361, 344, and 271 nm. Anal. Calcd for $C_{32}H_{21}N_2O_3Ga$ (%): C, 69.72; H, 3.84; N, 5.08. Found (%): C, 69.60; H, 3.70; N, 5.0. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.6.2. $(Acr)_2GaOC_6H_4OC_6H_{13}$ (2g). Orange solid. Yield: 37 mg (59%): m.p. >300°C. IR (KBr): ν 3056 (m), 2970 (m), 2861 (w), 1536 (m), 1147 (m), 1084 (m), and 732 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.15 (d, 2H, $J = 8.65$ Hz, $H^{8,8\prime}$), 9.00 (s, 2H, $H^{4,4\prime}$), 8.15 (d, 2H, $J = 8.51$ Hz, $H^{5,5\prime}$), 8.00 (t, 2H, $J = 8.23$ Hz, $H^{7,7\prime}$), 7.80 (t, 2H, $J = 8.51$ Hz, $H^{6,6\prime}$), 7.77 (t, 2H, $J = 6.72$ Hz, $H^{2,2\prime}$), 7.50 (d, 2H, $J = 6.73$ Hz, $H^{3,3\prime}$), 7.15 (d, 2H, $J = 7.82$ Hz, $H^{1,1\prime}$), 3.70 [t, 2H, $-OCH_2$], 1.20 [m, 8H, $-(CH_2)_4$], 0.87 [t, 3H, $-CH_3$] ppm. UV-Vis (CH_2Cl_2): λ_{max} (ϵ) = 453 (464), 363 (784), 346 (654), and 276 nm (9085 mol^{-1} dm^3 cm^{-1}). Anal. Calcd for $C_{38}H_{33}N_2O_4Ga$ (%): C, 70.07; H, 5.11; N, 4.30. Found (%): C, 69.70; H, 5.37; N, 4.05.

2.6.3. $(Acr)_2GaOCOC_6H_5$ (2h). Orange-red solid. Yield: 41 mg (73%): m.p. >300°C. IR (KBr): ν 3050 (m), 1626 (m, C=O), 1522 (m), 1407 (m), 1283 (m), 1147 (m), 1079 (m), 739 (s), and 620 (s) cm^{-1}. UV-Vis (CH_2Cl_2): λ_{max} = 446, 360, 343, and 272 nm. Anal. Calcd for $C_{33}H_{21}N_2O_4Ga$ (%): C, 68.42; H, 3.65; N, 4.84. Found (%): C, 68.30; H, 3.60; N, 4.72. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.6.4. $(Acr)_2GaOCOC_6H_4OC_6H_{13}$ (2i). Red solid. Yield: 44 mg (67%): m.p. >300°C. IR (KBr): ν 3053 (m), 2928 (m), 2868 (w), 1625 (m, C=O), 1536 (m), 1282 (m), 1148 (m), 1082 (m), 757 (s), and 732 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.10 (d, 2H, $J = 8.64$ Hz, $H^{8,8\prime}$), 9.00 (s, 2H, $H^{4,4\prime}$), 8.10 (d, 2H, $J = 8.23$ Hz, $H^{5,5\prime}$), 7.90 (t, 2H, $J = 7.68$ Hz, $H^{7,7\prime}$), 7.77 (d, 2H, $J = 8.65$ Hz, $H^{a,e}$), 7.52 (t, 2H, $J = 8.09$ Hz, $H^{6,6\prime}$), 7.50 (t, 2H, $J = 7.82$ Hz, $H^{2,2\prime}$), 7.40 (d, 2H, $J = 8.37$ Hz, $H^{3,3\prime}$), 7.20 (d, 2H, $J = 6.45$ Hz, $H^{b,d}$), 7.63 (d, 2H, $J = 8.64$ Hz, $H^{1,1\prime}$), 3.80 [t, 2H, $J = 7.28$ Hz, $-OCH_2$], 1.50 [m, 8H, $-(CH_2)_4$], 0.85 [t, 3H, $J = 6.59$ Hz, $-CH_3$] ppm. UV-Vis (CH_2Cl_2): λ_{max} = 453, 364, 343, and 276 nm. Anal. Calcd for $C_{39}H_{33}N_2O_5Ga$ (%): C, 68.94; H, 4.90; N, 4.12. Found (%): C, 69.29; H, 4.76; N, 4.12.

2.7. *Preparation of $(Acr)_2InZ$ (3f–3i)*

Complexes **3f**–**3i** were prepared as described for **2f**.

2.7.1. $(Acr)_2InOC_6H_5$ (3f). Orange solid. Yield: 40 mg (73%): m.p. >300°C. IR (KBr): ν 3059 (m), 1624 (m), 1518 (m), 1461 (m), 1282 (m), 1146 (m), 1080 (m), 749 (s), and 658 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 460$, 364, 347, and 279 nm. Anal. Calcd for

$C_{32}H_{21}N_2O_3In$ (%): C, 64.45; H, 3.55; N, 4.70. Found (%): C, 64.33; H, 3.42; N, 4.56. The poor solubility of this complex did not allow collection of ^1H NMR spectra.

2.7.2. $(Acr)_2InOC_6H_4OC_6H_{13}$ (3g). Red solid. Yield: 40 mg (62%): m.p. >300°C. IR (KBr): ν 3055 (m), 2965 (m), 2889 (w), 1566 (m), 1514 (m), 1359 (m), 1147 (m), 1080 (m), and 744 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.09 (d, 2H, $J = 8.95$ Hz, $H^{8,8\prime}$), 9.04 (s, 2H, $H^{4,4\prime}$), 8.21 (t, 2H, $J = 7.55$ Hz, $H^{5,5\prime}$), 8.16 (d, 2H, $J = 8.39$ Hz, $H^{a,e}$), 8.03 (t, 2H, $J = 7.58$ Hz, $H^{7,7\prime}$), 7.75 (t, 2H, $J = 8.33$ Hz, $H^{6,6\prime}$), 7.63 (d, 2H, $J = 8.36$ Hz, $H^{2,2\prime}$), 7.40 (d, 2H, $J = 8.20$ Hz, $H^{3,3\prime}$), 7.35 (d, 2H, $J = 7.29$ Hz, $H^{1,1\prime}$), 7.23 (d, 2H, $J = 7.21$ Hz, $H^{b,d}$), 3.56 [t, 2H, $-OCH_2$], 1.55 [m, 8H, $-(CH_2)_4$], 0.91 [t, 3H, $-CH_3$] ppm. UV-Vis (CH_2Cl_2): $\lambda_{max} = 475$, 366, 350, and 282 nm. Anal. Calcd for $C_{38}H_{33}N_2O_4In$ (%): C, 65.53; H, 4.78; N, 4.02. Found (%): C, 65.50; H, 4.60; N, 4.0.

2.7.3. $(Acr)_2InOCOC_6H_5$ (3h). Orange-red solid. Yield: 40 mg (69%): m.p. >300°C. IR (KBr): ν 3061 (m), 1625 (m, C=O), 1520 (m), 1397 (m), 1147 (m), 1080 (m), and 748 (s) cm^{-1}. UV-Vis (CH_2Cl_2): $\lambda_{max} = 462$, 363, 345, and 278 nm. Anal. Calcd for $C_{33}H_{21}N_2O_4In$ (%): C, 63.48; H, 3.39; N, 4.49. Found (%): C, 63.32; H, 3.21; N, 4.32. The poor solubility of this complex did not allow for ^1H NMR spectra.

2.7.4. $(Acr)_2InOCOC_6H_4OC_6H_{13}$ (3i). Bright red solid. Yield: 44 mg (65%): m.p. >300°C. IR (KBr): ν 3053 (m), 2955 (m), 2870 (m), 1623 (m, C=O), 1528 (m), 1282 (m), 1145 (m), 1080 (m), 763 (s), and 750 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.10 (d, 2H, $J = 9.06$ Hz, $H^{8,8\prime}$), 8.95 (s, 2H, $H^{4,4\prime}$), 8.05 (d, 2H, $J = 8.51$ Hz, $H^{5,5\prime}$), 7.90 (t, 2H, $J = 7.55$ Hz, $H^{7,7\prime}$), 7.90 (d, 2H, $J = 8.65$ Hz, $H^{a,e}$), 7.55 (t, 2H, $J = 7.82$ Hz, $H^{6,6\prime}$), 7.50 (t, 2H, $J = 7.55$ Hz, $H^{2,2\prime}$), 7.30 (d, 2H, $J = 8.37$ Hz, $H^{3,3\prime}$), 7.25 (d, 2H, $J = 7.21$ Hz, $H^{1,1\prime}$), 6.75 (d, 2H, $J = 8.64$ Hz, $H^{b,d}$), 3.90 [t, 2H, $J = 6.58$ Hz, $-OCH_2$], 1.65 [m, 8H $-(CH_2)_4$], 0.85 [t, 3H, $J = 6.87$ Hz, $-CH_3$] ppm. UV-Vis (CH_2Cl_2): $\lambda_{max} = 473$, 366, 349, and 282 nm. Anal. Calcd for $C_{39}H_{33}N_2O_5In$ (%): C, 64.65; H, 4.59; N, 3.87. Found (%): C, 64.76; H, 4.33; N, 3.60.

2.8. *Preparation of $(Acr)_2In(acac)$ (3l)*

An ethanolic solution (10 mL) of potassium acetylacetonate (26 mg, 0.186 mmol) was added to an ethanolic suspension (5 mL) containing **3a** (50 mg, 0.093 mmol). The resulting mixture was stirred for 24 h at reflux. After stirring the reaction mixture for 1 day, the precipitate was collected by filtration and repeatedly washed with water and ethanol. Recrystallization from chloroform : diethyl ether gave bright red **3l**. Yield: 35 mg (63%): m.p. >300°C. IR (KBr): ν 3060 (m), 1624 (m), 1536 (m), 1479 (m), 1458 (m), 1424 (m), 1147 (m), 1081 (m), 745 (s), and 731 (s) cm^{-1}. ^1H NMR ($CDCl_3$) : δ 9.37 (d, 2H, $J = 8.98$ Hz, $H^{8,8\prime}$), 8.79 (s, 2H, $H^{4,4\prime}$), 7.87 (d, 2H, $J = 8.54$ Hz, $H^{5,5\prime}$), 7.48 (t, 2H, $J = 7.69$ Hz, $H^{7,7\prime}$), 7.42 (t, 2H, $J = 7.26$ Hz, $H^{6,6\prime}$), 7.35 (t, 2H, $J = 7.96$ Hz, $H^{2,2\prime}$), 7.25 (d, 2H, $J = 7.37$ Hz, $H^{3,3\prime}$), 7.17 (d, 2H, $J = 7.65$ Hz, $H^{1,1\prime}$), 5.47 (s, 1H, –CH), 1.97 (s, 6H, $-CH_3$). UV-Vis (CH_2Cl_2): λ_{max} (ϵ) = 473 (361), 365 (241), 349 (301), and 282 nm (6566 mol^{-1} dm^3 cm^{-1}). Anal. Calcd for $C_{31}H_{23}N_2O_4In$ (%): C, 61.81; H, 3.85; N, 4.65. Found (%): C, 62.07; H, 3.74; N, 4.45.

2.9. *Preparation of [(Acr)$_2$In][CF$_3$SO$_3$] (3m)*

A solution of acetonitrile (5 mL) containing (trifluoromethylsulfonyloxy) silver (72 mg, 0.279 mmol) was added to **3a** (50 mg, 0.093 mmol) suspended in acetonitrile (5 mL). The resulting mixture was continuously stirred for 5 days at room temperature and then filtered on a Celite column. The filtrate was concentrated *in vacuo* and precipitated with diethyl ether, washed with diethyl ether and dried in vacuum. A green solid was obtained. Yield: 36 mg (60%): m.p. 201°C. IR (KBr): ν 3058 (m), 1622 (m), 1530 (m), 1278 (br, SO_3), 1174 (br, CF_3), 1077 (m), 733 (s), and 641 (s) cm^{-1}. ^{1}H NMR (CD_3CN): δ 8.98 (s, 2H, H$^{4,4\prime}$), 8.21 (d, 2H, $J = 8.07$ Hz, H$^{8,8\prime}$), 8.15 (d, 2H, $J = 8.51$ Hz, H$^{5,5\prime}$), 7.87 (t, 2H, $J = 6.60$ Hz, H$^{7,7\prime}$), 7.65 (t, 2H, $J = 6.60$ Hz, H$^{6,6\prime}$), 7.62 (d, 2H, $J = 7.48$ Hz, H$^{3,3\prime}$), 7.50 (t, 2H, $J = 7.34$ Hz, H$^{2,2\prime}$), 7.17 (d, 2H, $J = 7.34$ Hz, H$^{1,1\prime}$) ppm. UV-Vis (CH_3CN): $\lambda_{max} = 400$, 357, 340, and 256 nm. Anal. Calcd for $C_{27}H_{16}N_2O_5SF_3In$ (%): C, 49.71; H, 2.47; N, 4.29. Found (%): C, 49.44; H, 2.72; N, 4.0.

2.10. *Preparation of [(Acr)$_2$In(N,N)][CF$_3$SO$_3$] (3n, 3o)*

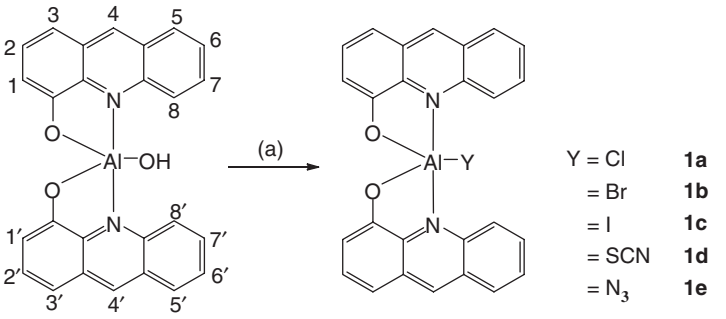
2.10.1. [(Acr)$_2$In(bipy)][CF$_3$SO$_3$] (3n). Complex **3m** (50 mg, 0.077 mmol) was dissolved in ethanol (5 mL) and a solution of 2,2′-bipyridine (60 mg, 0.383 mmol) in ethanol (5 mL) was added. The suspension was continuously stirred for 5 h at room temperature. The product was filtered and washed with ethanol and diethyl ether and dried in vacuum. A brown solid was obtained. Yield: 37 mg (59%): m.p. >300°C. IR (KBr): ν 3052 (m), 1525 (m), 1282 (br, SO_3), 1163 (br s, CF_3), 1082 (m), 783 (s), and 641 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.40 (d, 2H, $J = 9.15$ Hz, H^{a,h}), 9.04 (d, 2H, $J = 8.14$ Hz, H$^{8,8\prime}$), 8.96 (s, 2H, H$^{4,4\prime}$), 8.38 (t, 2H, $J = 7.92$ Hz, H^{b,g}), 8.01 (d, 2H, $J = 8.59$ Hz, H$^{5,5\prime}$), 7.84 (d, 2H, $J = 7.92$ Hz, H^{d,e}), 7.79 (t, 2H, $J = 7.41$ Hz, H$^{7,7\prime}$), 7.56 [m, 6H, H$^{c,f,2,2\prime}$, $^{6,6\prime}$], 7.35 (d, 2H, $J = 8.36$ Hz, H$^{3,3\prime}$), 7.20 (d, 2H, $J = 7.48$ Hz, H$^{1,1\prime}$) ppm. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 473 (524), 366 (1028), 349 (1129), and 279 (20080 mol^{-1} dm^3 cm^{-1}) nm. Anal. Calcd for $C_{37}H_{24}N_4O_5SF_3In$ (%): C, 54.97; H, 2.99; N, 6.93. Found (%): C, 54.78; H, 3.10; N, 6.72.

2.10.2. [(Acr)$_2$In(phen)][CF$_3$SO$_3$] (3o). Complex **3o** was prepared analogously as for **3m** using 1,10-phenanthroline. A brown solid was obtained. Yield: 38 mg (60%): m.p. >300°C. IR (KBr): ν 3055 (m), 1527 (m), 1281 (br, SO_3), 1172 (br, CF_3), 1076 (m), and 760 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.62 (s, 2H, H^{d,e}), 9.44 (s, 2H, H$^{4,4\prime}$), 8.59 (d, 2H, H^{a,h}), 8.42 (d, 2H, H$^{8,8\prime}$), 8.31 (d, 2H, H^{c,f}), 8.19 (t, 2H, H$^{7,7\prime}$), 8.03 (dd, 2H, H^{b,g}), 7.79 (d, 2H, H$^{5,5\prime}$), 7.68 (t, 2H, H$^{6,6\prime}$), 7.57 (t, 2H, H$^{2,2\prime}$), 7.35 (d, 2H, H$^{3,3\prime}$), 7.24 (d, 2H, H$^{1,1\prime}$) ppm. UV-Vis (CH_2Cl_2): $\lambda_{max} = 476$, 366, 348, and 282 nm. Anal. Calcd for $C_{39}H_{24}N_4O_5InSF_3$ (%): C, 56.27; H, 2.91; N, 6.73. Found (%): C, 56.20; H, 2.60; N, 6.55.

3. Results and discussion

3.1. *Aluminum complexes*

The HAcr ligand, treated with an equimolar amount of sodium hydroxide, reacted with Al(III) chloride giving a bright orange solid (80% yield) whose elemental analysis



Scheme 1. Proposed molecular structure and proton numbering scheme of the Al(III) complexes **1** and **1a**–**1e**. Reagents and conditions: LiCl or NaBr or KI or LiNSC or NaN_3, water : methanol, rt.

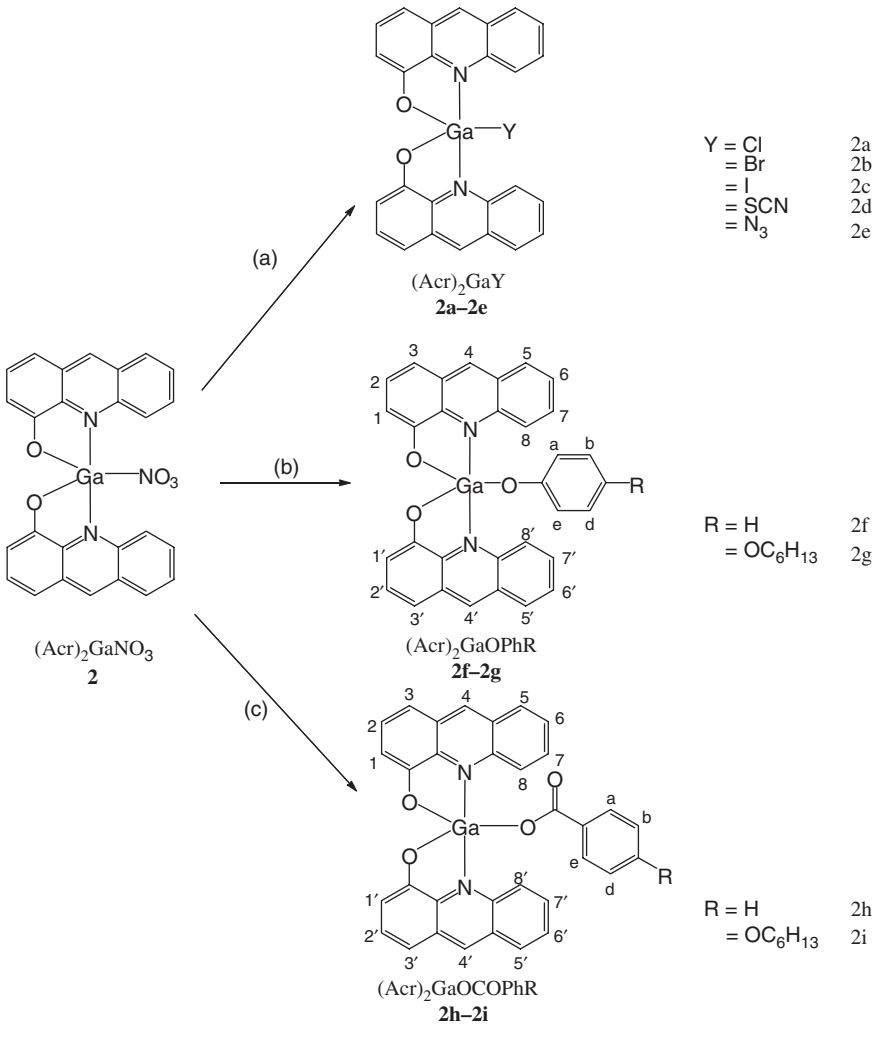
accounts for the hydroxo species $(Acr)_2AlOH$ (**1**). The molecular structure of **1** (scheme 1) was proposed from spectroscopic data with the IR spectrum showing, in the 1075–1143 cm^{-1} range, bands diagnostic of coordinated Acr and, at 2824 cm^{-1}, a strong band attributable to OH stretch. Likewise, ^1H NMR spectrum revealed the magnetic equivalence of two Acr moieties, the signals of which, with reference to HAcr, were shifted downfield upon coordination to Al(III).

Complex **1** undergoes metathetical reactions with substitution of OH for a monodentate ligand Y ($(Acr)_2AlY$; Y = Cl, Br, I, NCS, N_3, **1a**–**1e**, respectively, in scheme 1). Products **1a**–**1e** were characterized by elemental analysis. In addition, IR spectroscopy showed that the OH group disappeared in **1a**–**1e** and, for **1d** and **1e**, the appearance of a band attributable to NCS (2068 cm^{-1}, consistent with N-bonded isothiocyanato ligand) [10], or to the N_3 (2053 cm^{-1}) group [11], respectively. Complexes **1a**–**1e** are poorly soluble in standard solvents so that their ^1H NMR spectra are not available.

3.2. *Gallium complexes*

The Ga(III) source, $Ga(NO_3)_3 \cdot xH_2O$ reacted with HAcr in the presence of the required amount of NaOH to form $(Acr)_2GaNO_3$, **2** (scheme 2). This compound is a practically insoluble bright orange solid in 85% yield which gave satisfactory elemental analysis. The IR spectrum showed bands characteristic of both the coordinated Acr fragment (in the 1142–1085 cm^{-1} range) and NO_3 (at 1277 cm^{-1}). Complex **2** is a useful starting material for the synthesis of $(Acr)_2GaY$ (Y = Cl, Br, I, NCS, N_3, **2a**–**2e**, respectively, in scheme 2) which can be accomplished by treating **2** with an excess of MY (LiCl, NaBr, KI, LiNCS, and NaN_3). The actual stoichiometries of **2a**–**2e** were proved with elemental analysis and IR spectra confirmed the substitution of NO_3 for Y.

Another series of complexes containing the "$(Acr)_2Ga$" fragment, $(Acr)_2GaZ$ (**2f**–**2i**), was obtained (scheme 2) by reaction, in an alkaline medium, of **2** with some phenols (HZ = C_6H_5OH, **2f**, and $C_6H_{13}OC_6H_4OH$, **2g**) or carboxylic acids (HZ = C_6H_5COOH, **2h**, and $C_6H_{13}OC_6H_4COOH$, **2i**). These compounds, separated as orange (**2f** and **2g**) or red (**2h** and **2i**) solids (59%–73% yield) analyzing for $(Acr)_2GaZ$ with ^1H NMR spectra (available for **2g** and **2i** only) and IR spectra which displayed the expected features: e.g.

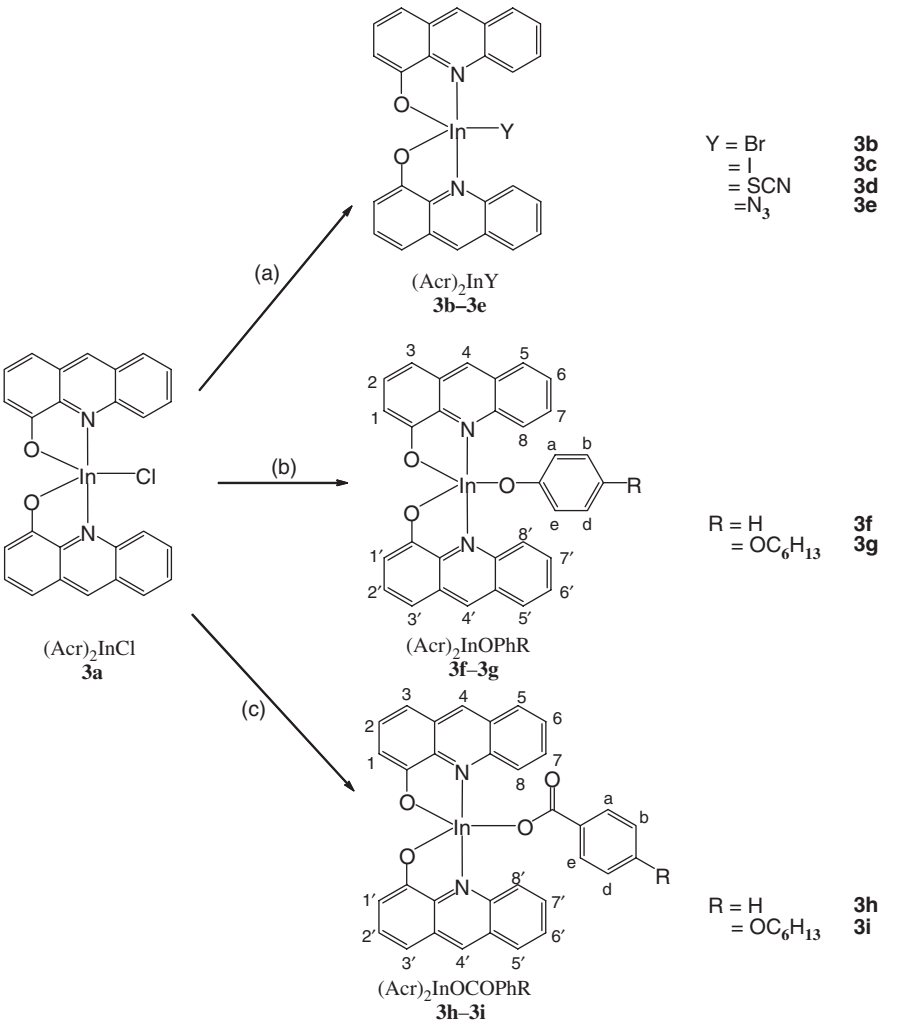


Scheme 2. Proposed molecular structure and proton numbering scheme of the Ga(III) complexes **2** and **2a**–**2i**. Reagents and conditions: (a) LiCl or NaBr or KI or LiNSC or NaN_3, water : ethanol or water : acetone, rt; (b) C_6H_5OH or $C_6H_{13}OC_6H_4OH$, water : ethanol, ΔT; (c) C_6H_5COOH or $C_6H_{13}OC_6H_4COOH$, water : ethanol, ΔT.

protonic resonances (which account for magnetically equivalent Acr fragments as illustrated by characteristic chemical shifts and relative intensities), IR aromatic absorptions between 1080 and 1140 cm^{-1} (**2f**–**2i**) and aliphatic CH stretches at 3050 cm^{-1} (**2g** and **2i**). The IR spectra also support the presence of monodentate carboxylate showing a band at 1626 and 1625 cm^{-1} for **2h** and **2i**, respectively [5c, 7a].

3.3. *Indium complexes*

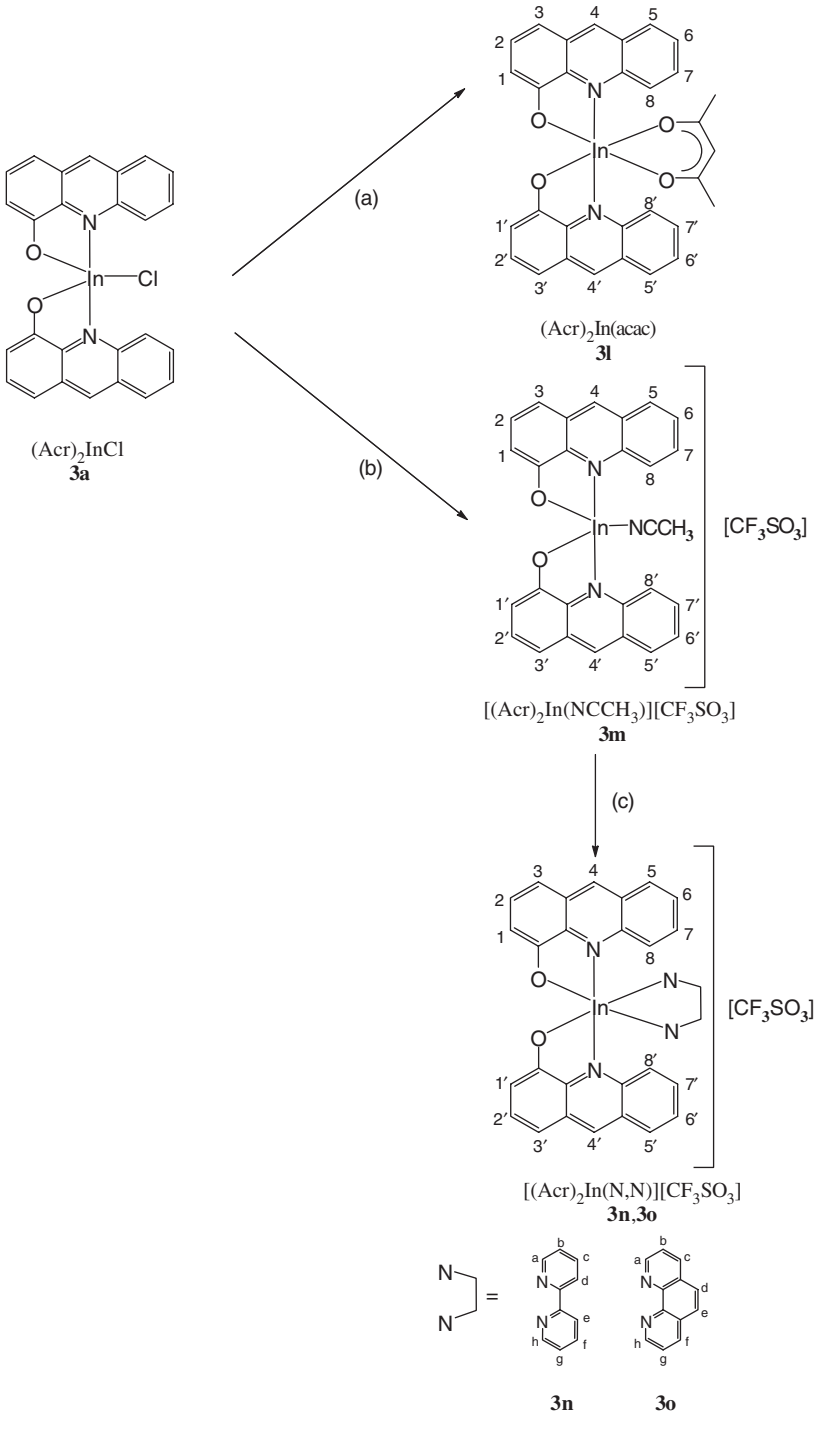
The HAcr ligand reacting in alkaline medium with $InCl_3$ gave a high yield (90%) of the pentacoordinated compound $(Acr)_2InCl$ (**3a**; scheme 3). This complex is an orange



Scheme 3. Proposed molecular structure and proton numbering scheme of the In(III) complexes **3a–3i**. Reagents and conditions: (a) LiCl or NaBr or KI or LiNSC or NaN_3, water : ethanol or water : acetone, rt; (b) C_6H_5OH or $C_6H_{13}OC_6H_4OH$, water : ethanol, ΔT; (c) C_6H_5COOH or $C_6H_{13}OC_6H_4COOH$, water : ethanol, ΔT.

solid of very low solubility in standard solvents, but characterized by stoichiometry and an IR spectral pattern in the 1146–1080 cm^{-1} range that reflects coordination of Acr.

The chloride present in **3a** can be easily replaced by a similar halide or pseudo-halide ligand (i.e. Br, I, NCS, or N_3, **3b–3e**, respectively, in scheme 3) through metathetical reactions. Moreover, like **2**, **3** reacts with phenols ($HZ = C_6H_5OH$ or $C_6H_{13}OC_6H_4OH$) or carboxylic acids ($HZ = C_6H_5COOH$ or $C_6H_{13}OC_6H_4COOH$) giving the respective orange compounds of $(Acr)_2InZ$, **3f–3i**. Elemental analyses of these compounds confirmed the calculated values and the IR and ^1H NMR (available for only **3g** and **3i**) spectra exhibit characteristics which parallel those for the homologous $(Acr)_2GaZ$ complexes (*vide supra*). The observed C=O stretching frequency (1625 cm^{-1} in **3h** and 1623 cm^{-1} in **3i**) indicated monodentate coordination of carboxylate.



Scheme 4. Proposed molecular structure and proton numbering scheme of the synthesized In(III) complexes **3l–3o**. Reagents and conditions: (a) Kacac, ethanol, ΔT; (b) $Ag[CF_3SO_3]$, acetonitrile, rt; (c) 2,2′-bipyridine or 1,10-phenanthroline, ethanol, rt.

A neutral hexacoordinate complex containing the "$(Acr)_2In$" fragment was obtained by treating **3a** with potassium acetylacetonato (**3l** in scheme 4). However, ionic hexacoordinate complexes required a two-step reaction, first by reacting **3a** with one equivalent of silver triflate (scheme 4) to form the solvato species $[(Acr)_2In(NCCH_3)][CF_3SO_3]$, **3m**, followed by addition of stoichiometric amounts of the neutral N,N chelating ligand (2,2′-bipyridine or 1,10-phenanthroline, respectively, bipy and phen, **3n** and **3o** in scheme 4). In addition to elemental analyses to characterize **3l**–**3o**, IR and ^1H NMR spectroscopic studies were also undertaken. For **3l**, IR spectrum showed strong band characteristics of the coordinated Acr fragment (1081–1147 cm^{-1}) and ^1H NMR spectrum revealed that the two Acr fragments are magnetically equivalent with a single set of signals for Acr. Moreover, confirmed by ^1H NMR, for **3l** partial dissociation of the acetylacetonato ligand was observed in solution.

For synthesis of **3m** it was necessary to replace the chloride with comparatively more labile CH_3CN, facilitating subsequent addition of N,N ligands. IR spectrum showed not only bands of triflate at 1278 and 1174 cm^{-1} [12] which confirm the ionic nature of **3m**, but also typical bands of coordinated Acr. Only one set of signals related to the magnetically equivalent Acr moieties was observed in the ^1H NMR spectrum.

The new complexes $[(Acr)_2In(bipy)][CF_3SO_3]$, **3n** and $[(Acr)_2In(phen)][CF_3SO_3]$, **3o**, are ionic hexacoordinated species whose IR spectra show bands for both the CF_3SO_3 group (1282 and 1163 cm^{-1} for **3n**; 1281 and 1172 cm^{-1} for **3o**) and those of Acr. ^1H NMR spectra showed that the two Acr fragments are magnetically equivalent and account for eight signals, while the other four signals correspond to the N,N ligand. For both **3n** and **3o** an octahedral coordination geometry, like that obtained by single crystal X-ray analysis for the homologous $[(MeQ')_2Ga(N,N)][PF_6]$ complexes (N,N = 2,2′-bipyridine or 1,10-phenanthroline) [9], can be proposed. Finally, free bipy and phen were present in solution, indicating the labile nature of these ligands to the "$(Acr)_2In$" fragment (^1H NMR evidence).

4. Conclusions

A new set of compounds was designed and synthesized to evaluate the complementary role that the steric hindrance of the HAcr and the ionic radius of Al(III)–In(III) triad have on the synthesis of 4-hydroxyacridinato complexes. The obtained results demonstrate that, despite the widespread tendency of these metals to prefer an octahedral coordination geometry, irrespective of the HAcr to M(III) molar ratio, HAcr gives rise to only $(Acr)_2MX$ species (**1**, **2**, and **3a**). Therefore, contrarily to HQ or HMeQ′, no $(Acr)_3M$ compounds are formed.

The starting materials **1**–**3** were successively reacted with homologous series of ligands which differed in steric demand and coordination capability. With halide or pseudo-halide Y ligands (Y=Cl, Br, I, NCS, N_3), pentacoordinated $(Acr)_2MY$ complexes were obtained. Complex **1** did not react with the more sterically demanding phenols HZ (HZ=C_6H_5OH and $C_6H_{13}OC_6H_4OH$), and the corresponding $(Acr)_2MZ$ derivatives could be obtained for only M=Ga and In. Similarly, with the carboxylato HZ ligands (HZ=C_6H_5COOH and $C_6H_{13}OC_6H_4COOH$), only pentacoordinated $(Acr)_2MZ$ compounds (M=Ga, In) with monodentate carboxylato coordination were isolated. Finally, hexacoordinated neutral ($(Acr)_2In(acac)$) or ionic

([$(Acr)_2In(bipy)$][CF_3SO_3] and [$(Acr)_2In(phen)$][CF_3SO_3]) complexes were obtained only with the larger In(III).

The reported investigation proves that interplay between the steric demand of the HAcr and the ionic radius along the Al(III), Ga(III), and In(III) triad allows synthesis of mixed ligand complexes containing two chelated 4-hydroxyacridinate ligands and a further ligand which could be used for addition of selected functionalities.

Acknowledgments

Financial support received from the Ministero dell'Istruzione, dell'Università e della Ricerca (MiUR) through the Centre of Excellence CEMIF.CAL (CLAB01TYEF) is gratefully acknowledged.

References

[1] (a) W.E. Ohnesorge, L.B. Rogers. *Spectrochim. Acta*, **14**, 27 (1959); (b) H. Schmidbaur, J. Lettenbauer, D.L. Wilkinson, G. Müller, O. Kumberger. *Z. Naturforsch.*, **46b**, 901 (1991); (c) L.S. Sapochak, A. Ranasinghe, H. Kohlmann, K.F. Ferris, P.E. Burrows. *Chem. Mater.*, **16**, 401 (2004).

[2] (a) C.W. Tang, S.A. VanSlyke. *Appl. Phys. Lett.*, **12**, 913 (1987); (b) C.W. Tang, S.A. VanSlyke, C.H. Chen. *J. Appl. Phys.*, **65**, 3610 (1989); (c) P.E. Burrows, L.S. Sapochak, D.M. McCarty, S.R. Forrest, M.E. Thompson. *Appl. Phys. Lett.*, **64**, 2718 (1994); (d) C.H. Chen, J. Shi. *Coord. Chem. Rev.*, **171**, 161 (1998); (e) L.S. Hung, C.H. Chen. *Mater. Sci. Eng. R*, **39**, 143 (2002).

[3] (a) U. Mitschke, P. Bäuerle. *J. Mater. Chem.*, **10**, 1471 (2000); (b) L.S. Sapochack, A. Padmaperuma, N. Washton, F. Endrino, G.T. Schmett, J. Marshall, D. Fogarty, P.E. Burrows, S.R. Forrest. *J. Am. Chem. Soc.*, **123**, 6300 (2001); (c) B.J. Chen, X.W. Sun, Y.K. Li. *Appl. Phys. Lett.*, **18**, 3017 (2003); (d) B.C. Lin, C.P. Cheng, Z. You, C. Hsu. *J. Am. Chem. Soc.*, **127**, 66 (2005).

[4] A. Yuchi, H. Hiramatsu, M. Ohara, N. Ohata. *Anal. Sci.*, **19**, 1177 (2003).

[5] (a) O. Popovych, L.B. Roger. *Spectrochim. Acta*, **16**, 49 (1960); (b) O. Popovych, L.B. Roger. *Spectrochim. Acta*, **21**, 1229 (1965); (c) L.S. Sapochak, P.E. Burrows, D. Garbuzov, D.M. Ho, S.R. Forrest, M.E. Thompson. *J. Phys. Chem.*, **100**, 17766 (1996).

[6] (a) P.R. Scherer, Q. Fernando. *Anal. Chem.*, **13**, 1938 (1968); (b) S.A. VanSlyke, P.S. Bryan, F.V. Lovecchio. US Patent No. 5, 150, 006 (1992); (c) P.S. Bryan, F.V. Lovecchio, S.A. VanSlyke. US Patent No. 5, 141, 671 (1992); (d) P. Moore, S.A. VanSlyke, H.J. Gysling. US Patent No. 5, 484, 922 (1996); (e) Y. Qiu, Y. Shao, D. Zhang, X. Hong. *Jpn. J. Appl. Phys.*, **39**, 1151 (2000); (f) L.M. Leung, W.Y. Lo, S.K. So, K.M. Lee, W.K. Choi. *J. Am. Chem. Soc.*, **122**, 5640 (2000); (g) I.S. Toulokhonova, I.A. Guzei, M. Kavana, R. West. *Main Group, Met. Chem.*, **25**, 489 (2002); (h) M. La Deda, I. Aiello, A. Grisolia, M. Ghedini, M. Amati, F. Lelj. *Dalton Trans.*, 330 (2006).

[7] (a) H. Schmidbaur, J. Lettenbauer, O. Kumberger, J. Lachmann, G. Müller. *Z. Naturforsch*, **46b**, 1065 (1991); (b) A. Elschener, H.W. Heuer, F. Jonas, S. Kirchmeyer, R. Wehrmann, K. Wussow. *Adv. Mater.*, **13**, 1811 (2001); (c) S. Tan, B. Zhao, Y. Zou, Z. Xiao, X. Wang, G. Yu, Y. Liu, D. Zhu. *J. Mater. Sci.*, **39**, 1405 (2004); (d) A. Crispini, I. Aiello, M. La Deda, I. De Franco, M. Amati, F. Lelj, M. Ghedini. *Dalton Trans.*, 5124 (2006).

[8] D.R. Lide, H.R. Frederikse. *CRC Handbook of Chemistry and Physics*, 76th Edn, CRC Press, Boca Raton (1995).

[9] A. Crispini, M. Ghedini, I. De Franco, I. Aiello, M. La Deda, N. Godbert, A. Bellusci. *Dalton Trans.*, 1186 (2008).

[10] (a) K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York (1986); (b) K. Vrieze, G. van Koten. In *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds), Pergamon, Oxford (1987).

[11] H. Sussek, F. Stowasser, H. Pritzkow, R.A. Fischer. *Eur. J. Inorg. Chem.*, 455 (2000).

[12] G.A. Lawrance. *Chem. Rev.*, **86**, 17 (1986).