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Group III quinaldates: synthesis, structure and photoluminescence

Christiana Birnara^a, Vadim G. Kessler^b and Giannis S. Papaefstathiou^a 💿

^aLaboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Zografou, Greece; ^bDepartment of Chemistry, Swedish University of Agricultural Sciences, Uppsala, Sweden

ABSTRACT

The reactions of Al(III), Ga(III) and In(III) nitrates with 2-quinaldic acid (qaH) afforded $[Al_2(OH)_2(qa)_4]\cdot 2H_2O$ (1), $[Ga(qa)_2(H_2O)_2]NO_3$ (2) and $[In(qa)_2(NO_3)(H_2O)]$ (3), respectively, in high yields. The crystal structures of 1, 2 and 3 have been determined by single-crystal X-ray crystallography. The structure of 1 features a di-hydroxo bridged $[Al_2(\mu-OH)_2]^{4+}$ dimer in which each Al(III) is further ligated by two bidentate chelate qa⁻ ligands. Complexes 2 and 3 are mononuclear with the M(III) ions in octahedral environments surrounded by two bidentate chelate qa⁻ and two H₂O in 2 or one H₂O and a terminal NO₃⁻ in 3. Characteristic IR as well as thermal analysis and solid-state fluorescence are discussed.

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Al(III) complexes; crystal structures; Ga(III) complexes; In(III) complexes; quinaldic acid; solid-state fluorescence



1. Introduction

Quinaldic acid (qaH), which is a biologically relevant molecule since it has been involved in the tryptophan's metabolism [1–3], is also a well-known organic precipitant for several,

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CONTACT Giannis S. Papaefstathiou 🖾 gspapaef@chem.uoa.gr

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mainly divalent, metal ions [4]. The ability of quinaldic acid to give insoluble or sparingly soluble metal complexes has been found useful for gravimetric analysis of such metal ions and/or for removing metal ions from aqueous solutions [4, 5]. To this end, several divalent guinaldate metal complexes (i.e. Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Ru^{II}, Pd^{II}, Cd^{II}, Hg^{II} and Pb^{II}) have been synthesized and characterized by single-crystal X-ray crystallography [6–31]. The anion of guinaldic acid (ga⁻) has also been found to stabilize several low valent metal ions (*i.e.* Cu¹, Rh^I and Ag^I) [32–37], lanthanide [38–40] and other trivalent metal ions (*i.e.* Cr^{III}, Fe^{III}, Bi^{III} and Os^{III}) [41–44] as well as several high valent metal ions (*i.e.* V^{IV}, V^V, Mn^V, Nb^V, W^{VI}, Re^V and Os^{IV}) [45–52]. Among them, only two group III quinaldate metal complexes have been structurally characterized, the mononuclear $[Ga(qa)_2Cl]$ [53] and the dinuclear $[Ga_2(OH)_2(qa)_4] \cdot 4py$ [5]. The first exhibits moderate antiproliferative activity against several human cancer cell lines and mouse fibroblasts while the second was isolated in an attempt to selectively remove Al³⁺ ions from acidic solutions containing a variety of other divalent metal ions and Cr³⁺. Despite the extended π -system of gaH and its monoanion ga⁻ there is only a handful of metal quinaldates where photophysical properties have been studied. These include few lanthanide [40, 54–57] and some metal(II) quinaldates [30].

Continuing our previous work on the coordination chemistry of group III metal complexes, which is focused on synthesis, structural characterization, spectroscopic study, evaluation of the biological activity and study of their photophysical properties [58–67], we report herein the synthesis, structural, spectroscopic characterization, thermal analysis and solid-state photoluminescence of three group III metal complexes, $[Al_2(OH)_2(qa)_4]\cdot 2H_2O$ (1), $[Ga(qa)_2(H_2O)_2]NO_3$ (2) and $[In(qa)_2(NO_3)(H_2O)]$ (3). Complexes 1 and 3 represent the first structurally characterized Al(III) and In(III) quinaldate complexes, while 2 is only the third structurally characterized quinaldate Ga(III) complex [5, 53].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions, using materials as received. Ga(NO₃)₃·9H₂O was prepared following literature procedures [60]. Microanalyses (C, H and N) were performed with an EA 1108 Carlo Erba analyzer. IR spectra were recorded on a Shimadzu FT/IR IRAffinity-1 spectrometer with samples prepared as KBr pellets. TGA diagrams were recorded on a Mettler-Toledo TGA/DSC1 instrument under a N₂ flow of 50 ml/min. Emission and excitation spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer on powdered samples dispersed and squeezed on a quartz plate.

2.2. Compound preparation

2.2.1. Synthesis of $[AI_{2}(OH)_{2}(qa)_{4}] \cdot 2H_{2}O(1)$

A solution of Al(NO₃)₃·9H₂O (90 mg, 0.24 mmol) in 10 mL DMF was added dropwise to a stirred solution of qaH (124 mg, 0.72 mmol) in DMF (10 mL). The resultant colorless solution was further stirred for 30 min and then left undisturbed at room temperature. Upon standing, X-ray quality colorless crystals of **1** formed over a period of one week. The crystals were collected by filtration, washed with DMF (1 × 5 mL) and Et₂O (1 × 5 mL) and dried in vacuum. Yield: 45 mg (46%), based on Al. Anal. Calcd for C₄₀H₃₀N₄O₁₂Al₂: C, 59.12; H, 3.72; N, 6.89.

Found: C, 59.23; H, 3.60; N, 6.94%. IR data (KBr pellets, cm⁻¹): 3547 m, 3447 br, 1683 s, 1661 s, 1618 m, 1596 m, 1515 w, 1461 m, 1375 s, 1342 s, 1189 m, 908 m, 820 m, 770 s.

2.2.2. Synthesis of [Ga(qa),(H,O),]NO₃(2)

A solution of Ga(NO₃)₃·9H₂O (109 mg, 0.26 mmol) in 15 mL MeOH was added dropwise to a stirred solution of qaH (128 mg, 0.74 mmol) in MeOH (10 mL). The resultant colorless solution was further stirred for 30 min and then left undisturbed at room temperature. Upon slow evaporation, X-ray quality colorless crystals of **2** formed over a period of three days. The crystals were collected by filtration, washed with MeOH (1 × 5 mL) and Et₂O (1 × 5 mL) and dried in vacuum. Yield: 130 mg (97%), based on Ga. Anal. Calcd for C₂₀H₁₆N₃O₉ Ga: C, 46.91; H, 3.15; N, 8.21. Found: C, 46.80; H, 3.02; N, 8.33%. IR data (KBr pellets, cm⁻¹): 3397 br, 3118 s, 3019 br, 1666 br, 1652 br, 1593 m, 1566 s, 1515 m, 1464 m, 1381 br, 1347 s, 1275 m, 1219 w, 1188 w, 1161 w, 972 s, 865 s, 779 s.

2.2.3. Synthesis of [In(qa),(NO₃)(H₂O)] (3)

A solution of $\ln(NO_3)_3$ ·5H₂O (80 mg, 0.20 mmol) in 10 mL MeOH was added dropwise to a stirred solution of qaH (100 mg, 0.58 mmol) in MeOH (10 mL). The resultant colorless solution was gently heated below the boiling point of MeOH (~50 C) and stirred for 15 min and then left undisturbed at room temperature. Upon slow evaporation, X-ray quality colorless crystals of **3** formed over a period of two days. The crystals were collected by filtration, washed with MeOH (1 × 5 mL) and Et₂O (1 × 5 mL) and dried in vacuum. Yield: 34 mg (31%), based on In. Anal. Calcd for C₂₀H₁₄N₃O₈In: C, 44.55; H, 2.62; N, 7.79. Found: C, 44.46; H, 2.50; N, 7.83%. IR data (KBr pellets, cm⁻¹): 3446 br, 3071 w, 1639 s, 1566 w, 1515 w, 1492 m, 1383 s, 1358 w, 1283 w, 1166 w, 902 w, 852 w, 805 w, 772 w.

2.3. Single-crystal X-ray crystallography

The data collections for single crystals of **1–3** were carried out at room temperature using MoK α radiation ($\lambda = 0.71073$ Å) on a Bruker SMART Apex-II diffractometer. Complete crystal data and parameters for data collection and processing are reported in table 1. The structures were solved by direct methods using SHELXS-97 [68] and refined by full-matrix least-squares techniques on F^2 with SHELXL-2014/7 [69].

3. Results and discussion

3.1. Brief synthetic comments

Complexes 2 and 3 were prepared by mixing a methanolic solution of qaH with a methanolic solution of a M(III) nitrate salt. The concentration of the resultant mixtures as well as the metal to ligand ratio do not seem to affect the identity of the products but they do change the reaction yields and most importantly the quality of the crystals. Complex 1 was prepared in the form of single-crystals in a similar fashion from a DMF solution. Although no base was added to the reaction mixtures, the quinaldic acid deprotonates to give quinaldate complexes most probably due to hydrolysis of the group III metal ions at very low pH [70]. Other attempts to obtain crystalline materials from aqueous solutions with or without the presence

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Compound reference	1	2	3
Empirical formula	C40H30AI2N4O15	$C_{20}H_{16}GaN_3O_9$	$C_{20}H_{14}InN_{3}O_{8}$
Temperature	¹⁰ 296(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2,/n	P2,/c
Unit cell dimensions	<i>a</i> = 8.9299(11) Å, <i>α</i> = 90°	<i>a</i> = 9.0096(1 ['] 7) Å, <i>α</i> = 90°	<i>a</i> = 10.271(2) Å, <i>α</i> = 90°
	b = 28.966(4) Å,	<i>b</i> = 5.9954(11) Å,	b = 9.905(2) Å,
	$\beta = 101.488(2)^{\circ}$	$\beta = 98.313(2)^{\circ}$	$\beta = 95.542(3)^{\circ}$
	<i>c</i> = 14.0526(18) Å, γ = 90°	$c = 20.335(4) \text{ Å}, \gamma = 90^{\circ}$	<i>c</i> = 19.528(4) Å, γ = 90°
Volume	3562.1(8) Å ³	1086.9(4) Å ³	1977.4(7) ų
Ζ	4	2	4
Density (calculated)	1.515 g cm ^{−3}	1.565 g cm ^{−3}	1.811 g cm ⁻³
Absorption coefficient	0.158 mm ⁻¹	1.323 mm ⁻¹	1.252 mm ⁻¹
F(0 0 0)	1680	520	1072
Crystal size	$0.30 \times 0.14 \times 0.12 \text{ mm}^3$	$0.39 \times 0.22 \times 0.08 \text{ mm}^3$	$0.32 \times 0.23 \times 0.19 \text{ mm}^3$
heta range for data collection	2.431 to 25.295°	3.546 to 25.245°	2.863 to 25.250°
Index ranges	$-10 \le h \le 10, -34 \le k \le 34,$	$-10 \le h \le 10, -7 \le k \le 7,$	$-12 \le h \le 12, -11 \le k \le 11,$
	−16 ≤ <i>l</i> ≤ 16	$-24 \le l \le 24$	-23 ≤ <i>l</i> ≤ 23
Reflections collected	15,216	9540	19,351
Independent reflections	$3223 [R_{int} = 0.0544]$	$1878 [R_{int} = 0.0381]$	$3554 [R_{int} = 0.0286]$
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
	on F ²	on F ²	on F ²
Data / restraints / parameters	3223 / 2 / 274	1878 / 180 / 169	3554 / 1 / 297
Goodness-of-fit	1.054	1.132	1.033
Final <i>R</i> indices $[l > 2\sigma(l)]$	$R_{\rm obs} = 0.0410,$	$R_{\rm obs} = 0.0636,$	$R_{\rm obs} = 0.0199,$
	$wR_{obs} = 0.0877$	$wR_{obs} = 0.1685$	$wR_{obs} = 0.0481$
R indices [all data]	$R_{all} = 0.0661, wR_{all} = 0.0977$	$R_{all} = 0.0694, wR_{all} = 0.1724$	$R_{\rm all} = 0.0264, wR_{\rm all} = 0.0498$
CCDC	1,512,454	1,512,455	1,512,456

Table 1. Crystal and structure refinement data for 1–3.

of a base (0.1 M NaOH) resulted in cloudy/milky suspensions from which we were not able to isolate any solid material by filtration.

3.2. Description of structures

Complex 1 crystallizes in the monoclinic space group C2/c and comprises a di-hydroxo bridged $[Al(\mu-OH)_{2}Al]^{4+}$ core (figure 1). The Al³⁺ centers and the μ -OH⁻ ligands are identical since a crystallographic twofold axis is passing through the center of the Al…Al distance, perpendicular to the [Al(µ-OH),Al]⁴⁺ mean plane. The di-hydroxo core is almost planar with both Al³⁺ and O being ~0.29 Å above or below the AlO₂Al mean plane with the AlOAlO torsion angle being 3.67°. The distorted octahedral environment around each metal center is completed by two N,O-chelate ga⁻ ligands having their nitrogens in trans orientation and their oxygens in *cis* orientation with respect to each other. The hydroxo O are *trans* and *cis* to the ga⁻ O and N, respectively. The Al···Al distance is 2.944(1) Å while the Al–O and Al–N distances are 1.844(2)-1.858(2) and 2.120(2)-2.132(2) Å, respectively. These values are comparable to previously characterized $[(L_{O,N})_2AI(\mu-OH)_2AI(L_{O,N})_2]$ dimers [71–75], where $L_{N,O}^-$ is the monoanion of a N,O-chelate ligand and shorter compared to the Ga…Ga, Ga–O and Ga-N distances in [Ga₂(OH)₂(qa)₄]·4py [5] due to the smaller effective ionic radius of Al³⁺ (Ga³⁺ 0.620 and Al³⁺ 0.535 Å) in an octahedral geometry [70]. Owing to their position around the dimer the qa⁻ ligands participate in intra-dimer π - π stacking interactions with the following parameters: centroid_{C5-C10}···centroid_{C5-C10} (-x, y, 0.5-z) 3.770(1) Å and centroid_{N2-} _{c20}···centroid_{c15-c20} (-*x*, *y*, 0.5-*z*) 3.515(1) Å.



Figure 1. The (Λ , Λ) isomer of the [Al₂(OH)₂(qa)₄] dimer in **1**. Dashed lines represent the π - π interactions (see text for details). Most hydrogens have been omitted for clarity. Color code: Al green, O red, N blue, C gray, H cyan. Symmetry code: (') –*x*, *y*, 0.5–*z*.



Scheme 1. The square and granny knots (top) and their analogy to the three possible isomers of $[(L_{0,N})_2 M(\mu-OH)_2 M(L_{0,N})_2]$ (bottom).

Symmetric dimers such as $[(L_{O,N})_2Al(\mu-OH)_2Al(L_{O,N})_2]$ have three possible isomers, the *meso* (Λ,Δ) and the *rac* $(\Delta,\Delta \text{ or }\Lambda,\Lambda)$ forms (scheme 1). The first is related to the square knot and is achiral, while the latter are related to the topological chiral granny knot that has two enantiomorphs [76]. Complex **1** comprises the *rac* form where both (Λ,Λ) and (Δ,Δ) enantiomorphs exist in the lattice. This is also the case in all other previously reported $[(L_{O,N})_2Al(\mu-OH)_2Al(L_{O,N})_2]$ dimers [71–74] except in one that comprises only one enantiomorph (the Δ,Δ) in its lattice [75]. The latter might precipitate as a conglomerate, but that has not been realized.



Figure 2. Representation of the real $(4^8.5^4.6^3)$ -**bsn** network adopted by **1**. Black spheres represent the $[Al_2(OH)_2(qa)_4]$ dimers, orange lines represent connections via $\pi - \pi$ stacking interactions and dashed black lines represent connections through the hydrogen bonding interactions.



Figure 3. The molecular structure and the hydrogen bonding interactions in **2**. Color code: Ga green, O red, N blue, C gray, H cyan. Symmetry code: (') 1-x, 1-y, -z, (") 1-x, 2-y, -z.

In the lattice, the molecules of **1** are connected with four neighboring molecules through intermolecular π - π interactions and to two other dimers via hydrogen bonding interactions that involve the bridging OH⁻, the uncoordinated carboxylate O4 and the lattice H₂O molecules (figure S1). In this arrangement, each dinuclear unit connects to six neighboring dimers creating a **bsn** network with point symbol (4⁸.5⁴.6³) (figure 2).

The mononuclear complex **2** crystallizes in the monoclinic space group $P2_1/n$. The Ga³⁺ is situated on a center of inversion and is in a distorted octahedral geometry surrounded by two bidentate chelate qa⁻ ligands and two terminal water molecules (figure 3). The qa⁻ ligands have both their N and O atoms in *trans* orientation forming the basal plane of the distorted octahedron with the terminal water molecules occupying the apical positions. The Ga-O_{qa}, Ga-N and Ga-O_{water} distances are 1.910(3), 2.123(4) and 1.987(4) Å, respectively. All *transoid*



Figure 4. The molecular structure and the weak interactions in **3**. Color code: In green, O red, N blue, C gray, H cyan. Most hydrogens have been omitted for clarity. Symmetry code: (') 2-x, 0.5 + y, 0.5-z, (") 2-x, 0.5-y, 0.5-z.

angles are 180°, but the *cisoid* angles related to the bite of the chelate qa^- ligand are acute (82.55°) with the rest around the basal plane being obtuse (97.45°). The water molecule forms almost right angles which range between 88.22° and 91.78° with the N and O of the qa^- ligands. In the lattice, the $[Ga(qa)_2(H_2O)_2]^+$ ions form a 1-D hydrogen-bonded chain along the *b* axis that involves the water molecule and the uncoordinated carboxylate O2 of the qa^- ligand with the following parameters: O3…O2 (1–*x*, 2–*y*, –*z*) 2.659(5) Å, H3B…O2 2.13 Å and ∠O3–H3B…O2 115°. The second hydrogen of the terminal water, H3A, is hydrogen bonded to the NO₃⁻ with the following parameters: O3…O4 2.562(9) Å, H3A…O4 2.18 Å and ∠O3–H3A…O4 104°. There are no other intermolecular interactions or π – π stacking in the crystal of **2**.

Complex 3 crystallizes in the monoclinic space group $P2_1/c$. It is also a mononuclear complex with the In³⁺ in a distorted octahedral geometry. Two bidentate chelate qa⁻ ligands having their N and O atoms in trans orientation, respectively, form the basal plane of the octahedron with the O atoms of a terminal NO₃⁻ and a terminal water molecule occupying the apical positions (figure 4). The In–O_{ga}, In–N, In–O_{nitrate} and In–O_{water} distances are 2.114(2), 2.099(2), 2.253(2), 2.283(2), 2.196(2) and 2.169(2) Å, respectively. These distances are longer than the respective bond distances in 2 due to the larger effective ionic radius of In(III) (In^{3+} 0.80 and Ga³⁺ 0.620 Å) in an octahedral geometry [70]. The *transoid* angles are within the 165.99° to 176.82° range while the cisoid angles fall within the range of 75.94° to 105.33°. In the lattice, the [In(qa)₂(NO₂)(H₂O)] molecules form a 1-D hydrogen-bonded chain along the b axis that involves the hydrogens of the terminal water and both the uncoordinated carboxylate O atoms of qa⁻ ligands with the following parameters: $O5 \cdots O2 (2-x, 0.5 + y, 0.5-z)$ 2.668(3) Å, H5B····O2 1.92(3) Å and ∠O5–H5B····O2 166(3)° and O5···O4 (2–x, y–0.5, 0.5–z) 2.692(3) Å, H5A···O2 1.93(2) Å and ∠O5–H5A···O4 170(4)°. The chain is further stabilized by intramolecular, intra-chain π - π interactions with the following parameters: centroid_{C5-} $_{C10}$ ··· centroid $_{C15-C20}$ (2-x, 0.5 + y, 0.5-z) 3.588(1) Å. Surprisingly, **2** and **3** are the first

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octahedral Ga(III) and In(III) complexes of any nuclearity comprising two N,O-chelate ligands with both N and O in *trans* orientation.

3.3. IR spectra

The IR spectrum of quinaldic acid exhibits a medium intensity band at ~1996 cm⁻¹ which is assigned to v(C=O) since qaH in the solid-state exists in two tautomeric forms, the neutral and the zwitterionic [77]. This band is apparent in the IR spectrum of **1** (1683 cm⁻¹) but not in the spectra of **2** and **3** (figure S2). The C–O distances of the uncoordinated carboxylate O in both crystallographically independent carboxylate units in **1** are shorter (1.214 Å) than the respective C–O distances of the uncoordinated carboxylate O in **2** (1.231 Å) and **3** (1.225 Å), implying a stronger character of the C=O bond in **1**. Quinaldic acid tautomers exhibit two $v_{as}(COO)$ and two $v_{s}(COO)$ bands at 1642, 1585, 1383, and 1317 cm⁻¹, respectively [26]. In the IR spectrum of **1** these bands are at 1661 cm⁻¹ and 1573 cm⁻¹ for $v_{as}(COO)$ and at 1375 cm⁻¹ and 1342 cm⁻¹ for $v_{s}(COO)$, respectively, while the IR spectra of **2** and **3** exhibit one antisymmetric (1662 cm⁻¹ in **2** and 1639 cm⁻¹ in **3**) and one symmetric (1347 cm⁻¹ in **2** and 1359 cm⁻¹ in **3**). The existence of the nitrates in the crystals of **2** and **3** is reflected in the appearance of a strong band at ~1384 cm⁻¹ [78]. The latter is absent in the spectrum of **1** due to the absence of nitrate ions in the crystal.

3.4. Thermal analysis

Thermogravimetric analysis (figure S3) reveals that **1** loses solvate water molecules from 65 to 135°C and degrades above 200°C. The residue at 600°C, 24.32%, is more than what is expected for Al_2O_3 (theoretical value 12.54%). Complex **2** loses coordinated water molecules from 130 to 145°C and degrades immediately after that. The residue at 600°C, 18.34%, corresponds to Ga_2O_3 (theoretical value 18.30%). Complex **3** loses coordinated water molecules



Figure 5. Excitation and emission spectra of 1–3 in the solid-state.

at 175–215°C and degrades above 300°C. The residue at 600°C, 36.82%, is more than what is expected for In₂O₃ (theoretical value 25.74%).

3.5. Solid-state photoluminescence measurements

The solid-state excitation and emission spectra of quinaldic acid and of **1–3** are shown in figure S4 and figure 5, respectively. Emission spectra were obtained after excitation at the peak maximum of the relevant excitation spectrum. Quinaldic acid exhibits an emission band with a maximum at 427 nm upon excitation at 366 nm. Complexes **1**, **2** and **3** exhibit emission maxima at 428 nm ($\lambda_{ex} = 327$ nm), 425 nm ($\lambda_{ex} = 370$ nm) and 436 nm ($\lambda_{ex} = 369$ nm), respectively, which are all within the blue light region. The maxima in the emission spectra of **1–3** are less broad but they are not significantly shifted compared to the emission of the free ligand. Since the emission of the complexes is ligand-based [30], the role of the M(III) atom is to impose conformational rigidity that restricts the energy loss via non-radiative decay [58].

4. Conclusion

A family of group III metal complexes based on the anion of quinaldic acid has been synthesized and structurally characterized. The Al(III) complex comprises a bis-hydroxo bridged core, surrounded by four chelate qa⁻ anions. The Ga(III) and In(III) complexes are mononuclear comprising an octahedral M(III) surrounded by two chelate qa⁻ ligands in *trans* orientation and solvent (H₂O for Ga) or H₂O and NO₃⁻ (for In). All complexes were also characterized by IR spectroscopy and thermal techniques. Both IR spectra and TGA are in agreement with the structures of the complexes. All complexes display ligand-based photoluminescence in the solid-state in the visible (blue) region. The emission maxima of all complexes are quite close to the ligand emission maximum, nevertheless, the intensity of the emission of the complexes is much higher than that of the free ligand. Complexes **1** and **3** are the first structurally characterized Al(III) and In(III) quinaldates while **2** is only the third structurally characterized Ga(III) quinaldate.

Supplementary material

CIF files of complexes 1-3 and figures.

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Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Giannis S. Papaefstathiou D http://orcid.org/0000-0001-5514-6371

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