Chapter 4

Ionic Hexacoordinated Gallium Compounds

4.1 Ionic Coordination Gallium(III) Compounds

Although ionic coordination gallium(III) compounds are attracting many attention due to their promising application in catalysis and in medicine, (Chapter 1, 1.4 paragraph) its are still rare compounds. Further heteroleptic hexacoordinated compound, synthesised with different chelating ligands, are unknown.

As reported in literature 2-methyl-8-hydroxyquinoline (HQ'), commonly named quinaldine, illustrated in **Figure 4.1**, reacting with gallium(III) salts in 3:1 molar ratio give the octahedral GaQ'_3 compound. While, with HQ':Ga in 2:1 molar ratio, in the presence of a third monodentate ligand (HL) it is possible to obtain pentacoordinated Gallium(III) compounds with Q'_2GaL stechiometry.[1]

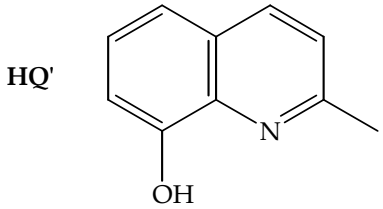
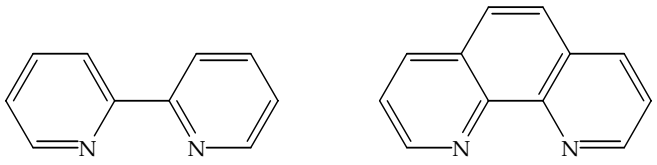


***Figure 4.1**: 2-methyl-8-hydroxyquinoline (HQ') or quinaldine.*

Following this synthetic approach an N,N bidentate ligand was taken in account as third ligand to achieve the hexacoordination.

The N,N ligands, 2,2'-bypiridine (bipy) and 1,10-phenanthroline (phen), illustrated in **Figure 4.2**, are largely used in the synthesis of charged metal complexes, and were also chosen because of their rigid aromatic structure.

The purpose was to synthesis gallium compounds of the general formula **[Q′$_2$Ga (N,N)][X]**.

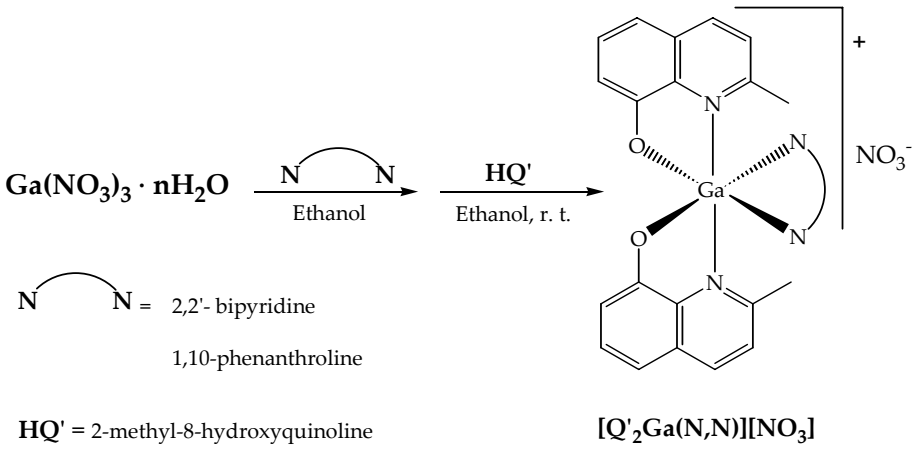


2,2'-bipyridine **1,10-phenanthroline**

Figure 4.2: *N,N ligands, 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen).*

4.2 Synthesis of charged hexacoordinated gallium(III) complexes

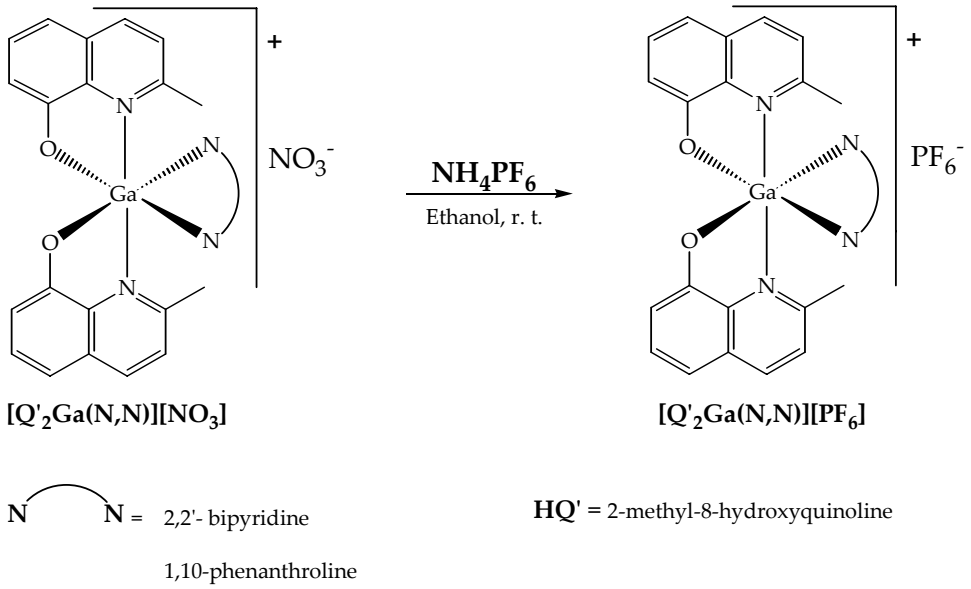
Hexacoordinated cationic gallium complexes **[Q′$_2$Ga(bipy)][X]** and **[Q′$_2$Ga(phen)][X]**, (X= NO_3^-, PF_6^-) were synthesised following the same procedure. An ethanol solution of 2,2′-bypiridine or 1,10-phenanthroline was added to an ethanol solution of gallium nitrate hydrate in the 1:1 molar ratio under stirring at room temperature. Hence an ethanol solution of 2-methyl-8-hydroxyquinoline (HQ′) was slowly dropped to the reaction mixture (molar ratio 2:1) as illustrated in **Scheme 4.1**.



Scheme 4.1: *synthesis of* ***[Q′$_2$Ga(bipy)][NO$_3$]*** *and* ***[Q′$_2$Ga(phen)][NO$_3$]****.*

The suspension was allowed to stir at room temperature overnight. A yellow powder was collected by filtration and washed with ethanol and diethyl ether so recrystallized from dichloromethane/diethyl ether. The yellow crystalline products were isolated in good yield and fully characterized.

The obtained complexes **[Q′$_2$Ga(bipy)][NO$_3$]** and **[Q′$_2$Ga(phen)][NO$_3$]** were solved in the minimum quantity of dichloromethane under stirring at room temperature then a solution of ammonium hexafluorophosphate (1:10 molar ratio) in acetone was added. This mixture was stirred at room temperature overnight to give a yellow suspension (**Scheme 4.2**).



Scheme 4.2: *synthesis of* ***[Q′$_2$Ga(bipy)][PF$_6$]*** *and* ***[Q′$_2$Ga(phen)][PF$_6$]***.

The **[Q′$_2$Ga(bipy)][PF$_6$]** and **[Q′$_2$Ga(phen)][PF$_6$]** complexes were obtained as yellow powders in good yield. Infrared spectra show the methyl group stretching around 3063 cm^{-1} for **[Q′$_2$Ga(bipy)][NO$_3$]** and **[Q′$_2$Ga(phen)][NO$_3$]** complexes while it is shifted around 3070 cm^{-1} for the **[Q′$_2$Ga(bipy)][PF$_6$]** and **[Q′$_2$Ga(phen)][PF$_6$]**.

Characteristic bands of the chelated 2-methyl-8-hydroxyquinolinate (*Q′*) profile are observed in the 1610-1030 cm^{-1} range for all complexes. The presence of the

NO_3^- and PF_6^- counter ions is revealed by the intense bands at 1384 cm^{-1} and 845 cm^{-1} respectively.[2] In **Figure 4.3** it is possible to observe the ^1H NMR of **[Q′$_2$Ga(N,N)][X]** compounds .

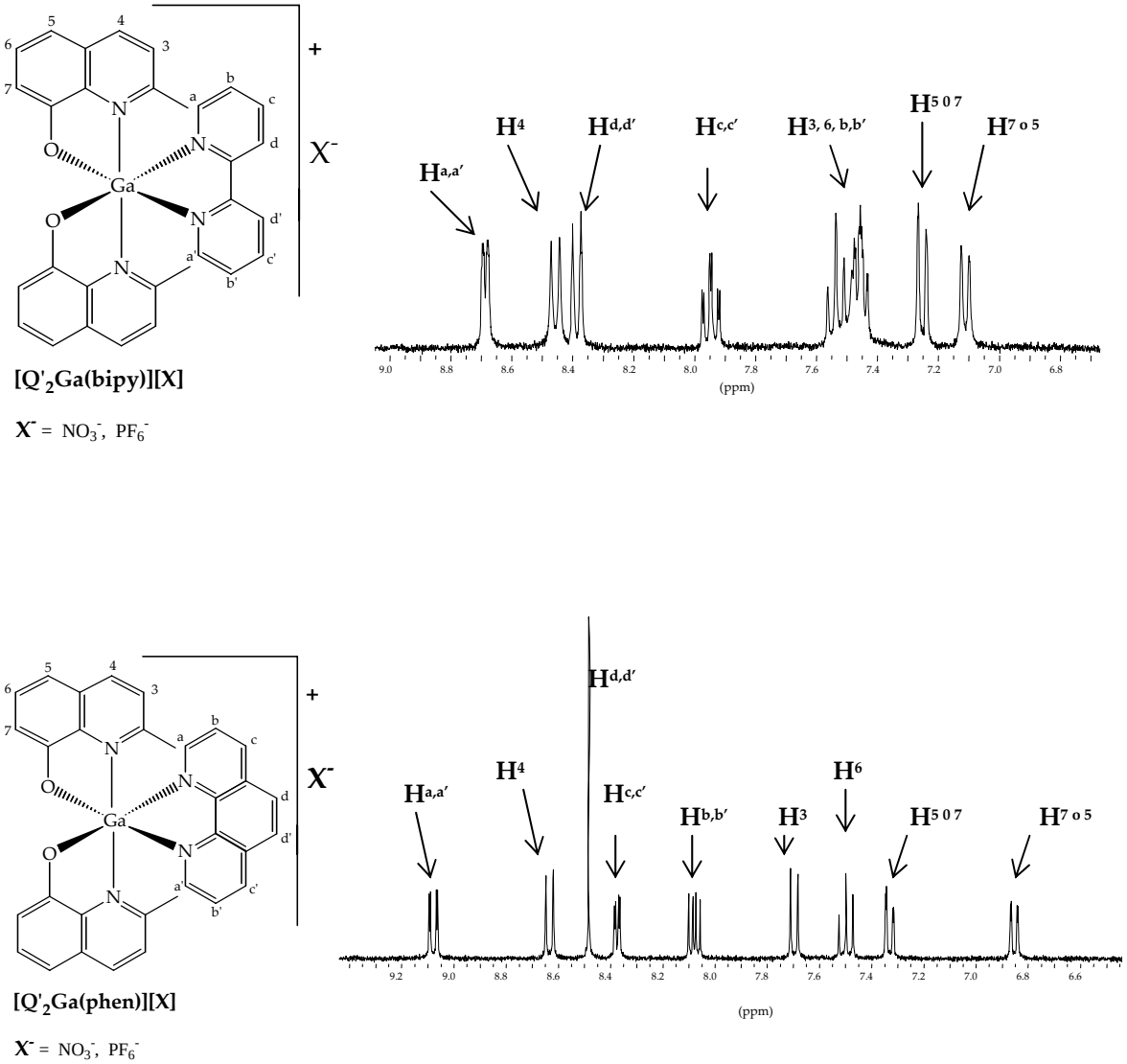


Figure 4.3: *^1H NMR of* ***[Q′$_2$Ga(bipy)][X]*** *and* ***[Q′$_2$Ga(phen)][X]*** *compounds.*

The protons of the two 2-methyl-8-hydroxyquinoline moieties show only one set of signals for all complexes, revealing their magnetic equivalence. In ^1H NMR spectra of **[Q′$_2$Ga(bipy)][X]**, the $H^{d,d'}$ and $H^{c,c'}$ signals are slightly shifted to lower frequencies respect to those of the unchelated bipyridine. ^1H NMR spectra of **[Q′$_2$Ga(phen)][X]** show $H^{a,a'}$ and $H^{c,c'}$ signals slightly shifted to low

fields while $H^{d,d'}$ and $H^{b,b'}$ to higher fields respect the chemical shift of the unchelated phenanthroline protons. Comparing the two spectra, the presence of the 1,10-phenanthroline, more rigid and more extended aromatic system, influence the shift to higher frequencies of all quinaldinate protons. These results were registered in acetone were these compounds show chemical stability. In fact previous ^1H NMR analysis in DMSO-d_6 for both compounds revealed each time the dissociation of the phenanthroline and bipyridine ligands as reported in **Figure 4.4**.

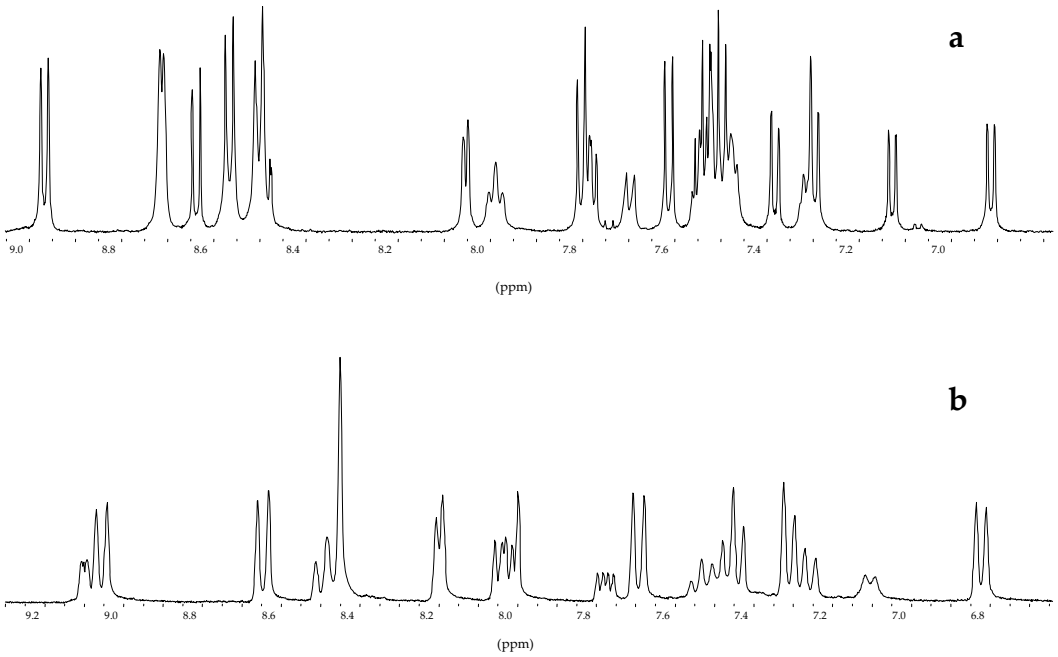


Figure 4.4: ***a)*** *^1H NMR of the dissociated* ***[Q'$_2$Ga(bipy)][X]*** *compounds;* ***b)*** *^1H NMR of the dissociated* ***[Q'$_2$Ga(phen)][X]*** *compounds.*

Only the proton signals related to the N,N ligands are affected of this behaviour while the *Q'$_2$Ga-* proton signals are unchanged. **[Q'$_2$Ga(phen)][X]** compounds show the same behaviour also in $CDCl_3$ probably, because of the rigidity of 1,10-phenanthroline, the coordination with the metal centre is tensioned and can be threaten also by slightly coordinating solvents. However, in order to explain this behaviour and to avoid the probability of the presence of isomers or

unreacted ligands, the syntheses were carried out following different pathways for examples aqueous solutions with high (-100 °C) or low (-20 °C) temperatures were adopted, in all case only the desired products were collected and the competitive formation of the neutral hexacoordinated complexes GaQ'_3 wasn't detected.[3] Always the same pure products, here described, were obtained. All compounds were analysed by differential scanning calorimetry (DSC) revealing absence of polymorphysm depending on temperature.

X-ray diffraction on single crystals of **[Q'$_2$Ga(N,N)][X]** complexes, obtained from dichloromethane/diethyl ether or dichloromethane/ethanol solutions, completed the solid state characterization. **Figure 4.5** shows only the complexes **[Q'$_2$Ga(N,N)]$^+$** cations and the selected atom-labelling scheme. Structures and crystal packing are still under investigation.

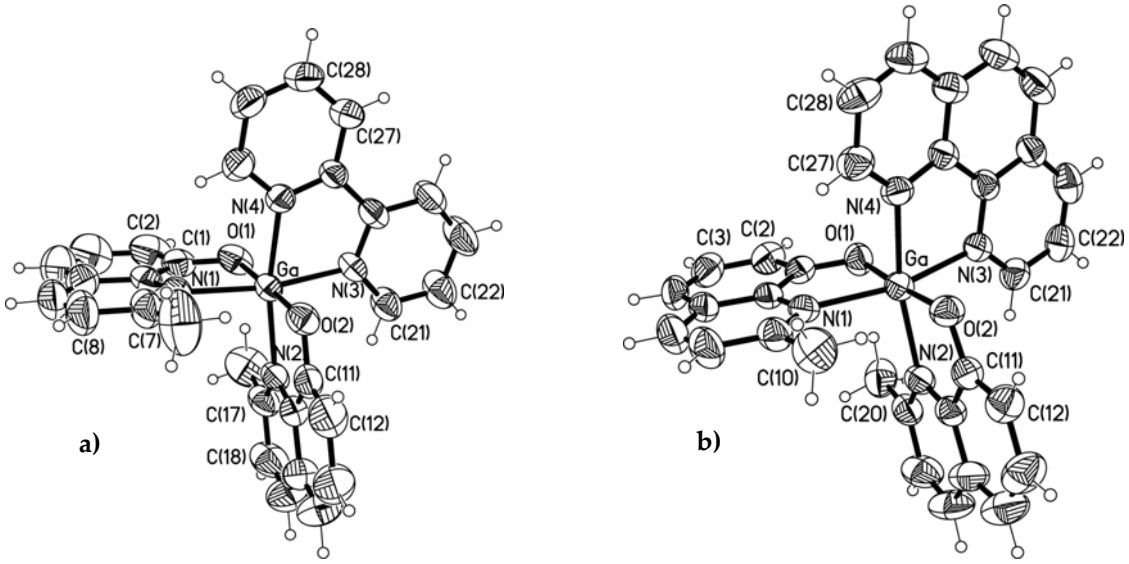


Figure 4.5: *Perspective view of the complexes of a)* ***[Q'$_2$Ga(bipy)][X]*** *and b)* ***[Q'$_2$Ga(phen)][X]*** *cations with atomic numbering scheme (ellipsoids at the 50% level).*

In all cases, the **[Q'$_2$Ga(N,N)][X]** complexes contain a hexacoordinated gallium center. The angles around the Ga(III) ion approximate an octahedral geometry, with the two Q'_2 ligands in an O,O *trans* conformation (O–Ga–O angle ranges from 176.3 to 178.6°). The N,N aromatic ligands complete the coordination

sphere, chelating the Ga(III) ion with both nitrogen atoms *trans* to the Q'_2 ligands nitrogen.

GaQ'_3 is significantly less stable in air than other tris-quinolinate compound MQ_3, or Q'_2ML compounds where M is aluminium(III) or gallium(III). Under ambient conditions their chemical stability could be threaten by oxygen and water both in solution and in the solid state. The greater steric hindrance, due to the methyl group in the second position of the quinaldinate moiety in GaQ'_3, may be responsible for the lowered stability relative to GaQ'_3 and Q'_2GaL compounds.[4]

In order to have an idea about the chemical stability of the ionic gallium compounds, a series of tests on **$[Q'_2Ga(N,N)][PF_6]$** complexes were performed in solution. A dichloromethane solution, $1x10^{-4}$ M, of the synthesised compounds was dropped into a cuvette containing cyclohexane with a Gilson pipette. The drops, 0.5 µL, were added each minutes and half. Cyclohexane was chosen because of this solvent can contain small amount of water that in an organic apolar solvent can be a strong nucleophil. When the degradation became evident the UV absorption spectra of this bisquinaldinate gallium compounds show the progressive enhancement of absorption band at 245 nm characteristic of the unchelated 2-methyl-8-hydroxyquinoline. So thirty additions, then thirty absorption spectra for each compound were recorded as illustrated in **Figure 4.6**.

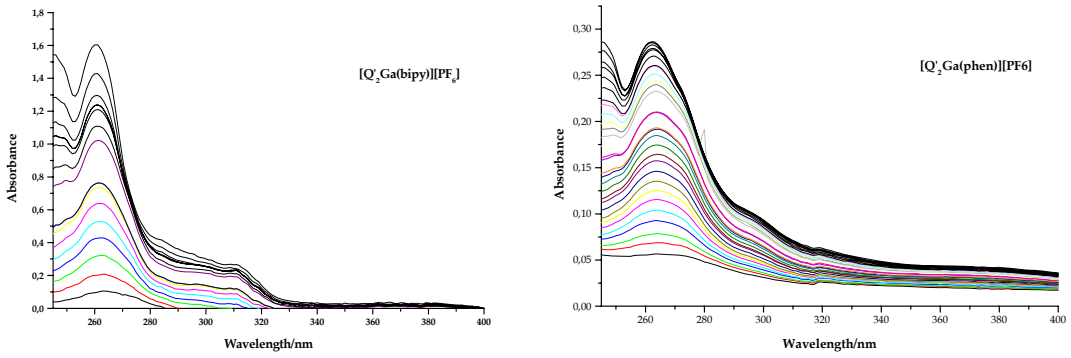


Figure 4.6: *absorption spectra of* ***$[Q'_2Ga(bipy)][PF_6]$*** *and* ***$[Q'_2Ga(phen)][PF_6]$*** *in cyclohexane.*

The ratio of the band absorption maximum at 245 nm and at 260 nm (typical of the bisquinaldinate gallium compounds), **A_{245}/A_{260}**, were plotted versus the timescale of the drop additions, as reported in the **Figure 4.7**.

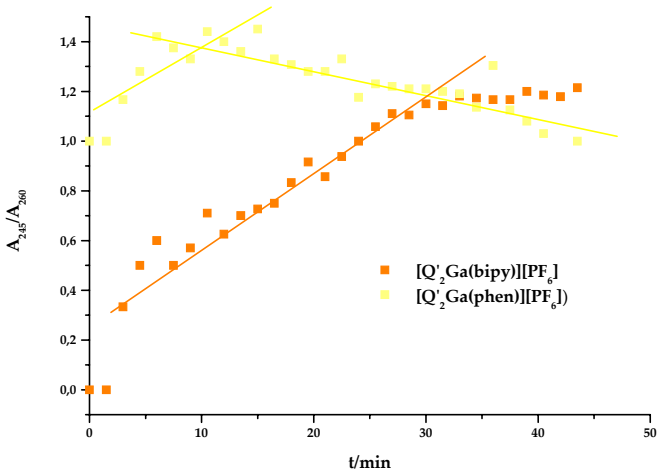


Figure 4.7: *A_{245}/A_{260} versus timescale drop addition graphs.*

The value of **A_{245}/A_{260}** ratio increase when the absorption band at 245 nm grows in intensity. The ratio remain almost a constant value when substantial changes in the absorption values are not observed. Comparing the graphs in **Figure 4.7**, the compounds that shows better stability in the described environmental conditions is **[Q′$_2$Ga(bipy)][PF$_6$]**.

The displacement of the 2-methyl-8-hydroxyquinoline ligand is a mechanism slower than those showed by **[Q′$_2$Ga(phen)][PF$_6$]** solutions

4.3 Photophysical characterization

Informations about the luminescent behaviour of cationic gallium complexes are very rare. In the present study absorption and emission spectra of **[Q′$_2$Ga(N,N)][X]** compounds, were collected in dichloromethane solutions and

on KBr pellets. Photoluminescent quantum yields, Φ_{PL}, were calculated using $[Ru(bipy)_3]Cl_2$, (H_2O, Φ_{PL}= 0,028) as standard. In **Figure 4.8** are shown the absorption and the emission spectra of **[Q'$_2$Ga(bipy)][X]** compounds.

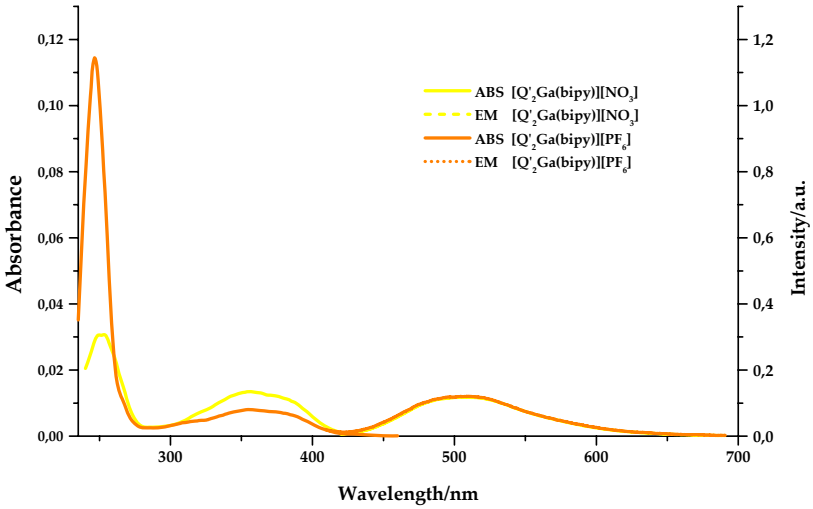


Figure 4.8: *absorption and emission spectra of* ***[Q'$_2$Ga(bipy)][X]****.*

As reported in **Table 4.1**, absorption and emission spectra of **[Q'$_2$Ga(bipy)][X]**, display an intense absorption band at 260 nm, typical of π–π* in the *Q'$_2$Ga*-compounds,[3] red shifted at 270 nm in KBr. Their presence could means that the HOMO-LUMO transitions are centred on the bisquinaldinate moiety. The emission spectra collected in solutions show emission centred at 505 nm and an hypsochromic shift about of 15 nm. As it can be noted the photoluminescence quantum yield is strongly reduced with **[Q'$_2$Ga(bipy)][PF$_6$]**.

[Q'$_2$Ga(bipy])[X]	*CH_2Cl_2 solutions*		*KBr pellets*	
	Absorbance λ/nm, (ε/M^{-1}cm^{-1})	*Emission* λ/nm ($^a\Phi_{PL}$)*	*Absorbance λ/nm*	*Emission* λ/nm*
[Q'$_2$Ga(bipy)][NO$_3$]	260(5255), 370(293)	505, (0.25)	270, 390	490
[Q'$_2$Ga(bipy)][PF$_6$]	260(17241), 370(924)	507, (0.04)	270, 390	490

*λ_{ex} = 375 nm

Table 4.1: *photophysical data in solution and on KBr of* ***[Q'$_2$Ga(bipy)][X]****.*

In the absorption spectra of **[Q'$_2$Ga(phen)][X]** compounds the only difference, respect to the analogues compounds with bipyridine, is the presence of a shoulder at 295 nm as it can be observed in **Figure 4.9**. The emission maximum values, collected in solution, are slightly red-shifted respect those of **[Q'$_2$Ga(bipy)][X]** while any substantial difference is observed on KBr.

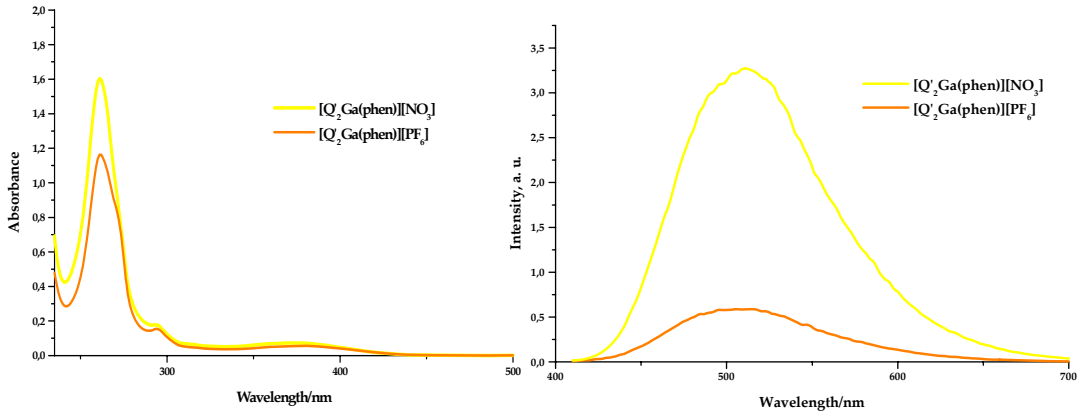


Figure 4.9: *absorption and emission spectra of* ***[Q'$_2$Ga(phen)][X]****.*

Furthermore, a dramatic quenching is evidenced in the compound bearing the PF_6^- anion as evidenced previously in the analogue compounds synthesised with bipyridine. The photophysical data of **[Q'$_2$Ga(phen)][X]** complexes are reported in **Table 4.2**.

[Q'$_2$Ga(phen)][X]	*CH_2Cl_2 solutions*		*KBr pellets*	
	Absorbance ***λ/nm,*** *(ε/$M^{-1}cm^{-1}$)*	***Emission**** ***λ/nm*** *($^a\Phi_{PL}$)*	***Absorbance*** ***λ/nm***	***Emission**** ***λ/nm***
[Q'$_2$Ga(phen)][NO$_3$]	260(28237) 295(3021), 370(1312)	510, (0.15)	270, 390	490
[Q'$_2$Ga(phen)][PF$_6$]	260(57500) 295(7500), 370(2700)	510, (0.04)	270, 390	490

*λ_{ex} = 375 nm

Table 4.2: *photophysical data in solution and on KBr of* ***[Q'$_2$Ga(N,N)][X]****.*

4.5 Cyclovoltammetric characterization

Cyclic voltammograms (CV) of complexes **[Q'$_2$Ga(bipy)][PF$_6$]** and **[Q'$_2$Ga(phen)][PF$_6$]** have been recorded in dry dichloromethane solutions containing tetrabutylammonium hexafluorophosphate (0,1M) as supporting electrolyte. Ferrocene was used as internal standard, and all potentials are referenced versus Fc^+/Fc couple, Pt working electrode *vs.* Ag/Cl as reference electrode. These complexes comprising a redox inactive gallium(III) ion show a ligand-based redox activity. Both compounds are oxidised and reduced at the same potentials with the only difference that reduction of **[Q'$_2$Ga(bipy)][PF$_6$]** is reversible while for **[Q'$_2$Ga(phen)][PF$_6$]** is completely irreversible, as illustrated in **Figure 4.10**, suggesting that the more rigid character of the phenanthroline ligand with respect to the bipyridine, destabilised more drastically the reduced complex.

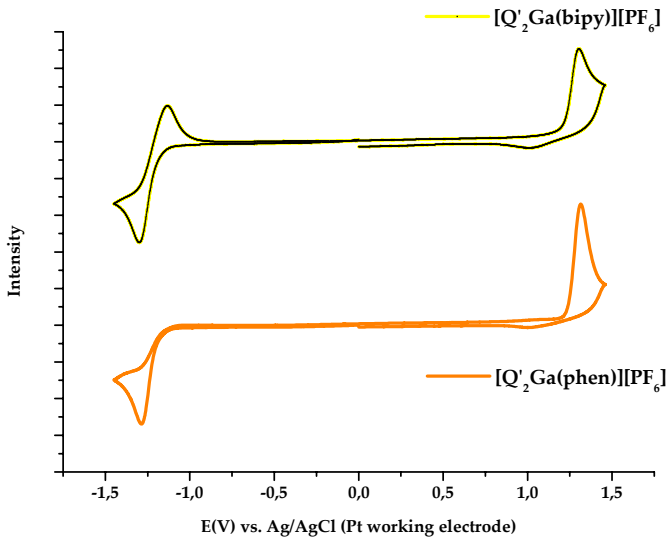


Figure 4.10: *cyclovoltammetries of* ***[Q'$_2$Ga(bipy)][PF$_6$]*** *and* ***[Q'$_2$Ga(phen)][PF$_6$]***

As reported in **Table 4.3**, the HOMO energy level, estimated by cyclic voltammetry for the two ionic complexes, is 5,74 eV, while the LUMO energy

level is 3,2 eV for **[Q′$_2$Ga(bipy)][PF$_6$]** and 3.14 eV for **[Q′$_2$Ga(phen)][PF$_6$]** compounds.

[Q′$_2$Ga(N,N)][PF$_6$]	*E^{ox} (V) vs. Fc$^+$/Fc*	*E^{red} (V) vs. Fc$^+$/Fc*	*HOMO (eV)*	*LUMO (eV)*	*Band Gap (eV)*
[Q′$_2$Ga(bipy)][PF$_6$]	+ 0,94 (Irr.)	- 1,60 (Rev.)	- 5,74[b]	- 3,2[b]	2,54
[Q′$_2$Ga(phen)][PF$_6$]	+ 0,94 (Irr.)	-1,66 (Irr.)	- 5,74[b]	- 3,14[b]	2,6

[b]*Values calculated using - 4.8 eV for ferrocene.*

Table 4.3: *cyclic voltammetric data of* ***[Q′$_2$Ga(N,N)][PF$_6$]****.*

4.6 Conclusions

New ionic hexacoordinated gallium complexes with the general formula **[Q′$_2$Ga(N,N)][X]**, (N,N= 2,2′-bypiridine (bipy) and 1,10-phenanthroline (phen) (X= NO_3^-, PF_6^-) were synthesised, noteworthy charged bis-quinaldinate gallium(III) compounds are unknown in literature.

These complexes are obtained as yellow powders at list at 50% reaction yields. Thermal analysis reveals the absence of polymorphism. All complexes show solubility in dichoromethane, DMSO and acetone. But some chemical instability could arise in coordinating solvents as evidenced in the ^{1}H NMR spectra collected in DMSO and $CDCl_3$ for **[Q′$_2$Ga(phen)][X]** complexes. Furthermore, in case of technological application its could be sensible to ambient moisture as typically showed by the quinolinate metal complexes. X-ray diffraction on single crystal confirm the hexacoordination approximating an octahedral geometry. The photophysical results linked with the CV data suggest that the HOMO energy distribution of **[Q′$_2$Ga(N,N)][X]** is probably distributed on the quinolate fragments.

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