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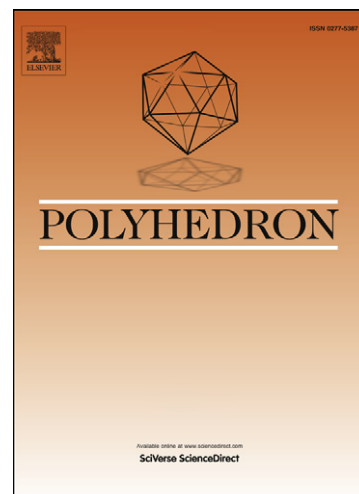
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Theoretical and experimental insights into the complexation of 8-hydroxyquinoline-5-sulfonate with divalent ions of Group 12 metals^Y

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^Y This article is dedicated to Professor Alfred Werner, the father of coordination chemistry.

ABSTRACT

The complexation of 8-hydroxyquinoline-5-sulfonic acid with cadmium(II) and mercury(II) has been studied in aqueous solutions using UV/visible absorption, fluorescence and ^1H NMR spectroscopy, accompanied by DFT calculations. Results are compared with the behaviour of zinc(II) and show in all cases the dominant formation of a 1:2 (metal:ligand) complex. DFT calculations under PCM (water) conditions indicate a preference for hexacoordinated metal centres with two ligands and two water molecules. However, while the zinc(II) complex has a square bipyramidal geometry, with the two 8-HQS ligands and metal in the same plane and two coordinated water molecules mutually *trans*, with cadmium(II) and mercury(II), the isomers in which the water molecules are in the *cis* geometry are more stable. Changes in UV/visible absorption, fluorescence spectra and fluorescence intensity are observed on complexation. Fluorescence quantum yields follow the order $\text{Zn}/8\text{-HQS} < \text{Cd}/8\text{-HQS} > \text{Hg}/8\text{-HQS}$. We believe two competing factors may be involved: an increase in fluorescence on going from Zn(II) to Cd(II) due to increased stability, and a decrease on going increasing atomic number of the metal ion due to the heavy atom effect which increases intersystem crossing. Triplet state quantum yields were measured for the Zn(II) and Cd(II) complexes, and the value for the cadmium(II) complex is higher, in agreement with the heavy atom effect. However, the sum of fluorescence and triplet quantum yields in these cases is less than unity. It is suggested that there is a competing non-radiative route for deactivation of the excited state through ligand or solvent exchange. This provides a ready explanation of increased fluorescence yields when metal/8-HQS complexes are immobilized in solid matrices.

1. Introduction

The group 12 metals zinc, cadmium and mercury share a common divalent oxidation state and also show many similarities in their coordination chemistry [1]. However, while zinc is an essential element for humans, animals and plants, and plays a central role in regulating cellular metabolism [2,3], cadmium and mercury are both toxic heavy metals, and are being subject to increasing legislation worldwide to prohibit or limit their use [4]. Nevertheless, cadmium and mercury or their compounds have been extensively used for a variety of technological applications. For example cadmium has been widely used in rechargeable nickel-cadmium batteries, CdS was until recently an important red pigment, while mercury is still extensively used in fluorescent tubes for lighting. These are persistent species in the environment, and there is strong current interest in the development of methods for both their detection and elimination from the environment [5]. Most of these are based upon appropriately designed metal chelates.

8-hydroxyquinoline (8-HQ) and its derivatives represent one of the most important and versatile chelating agents for many applications. These complex with a wide variety of cations, and have found a broad spectrum of applications, including light emitting diodes (LEDs) [6], complexants for radionuclides in nuclear medicine [7] and biomedical uses in treating cancer [8] or neurodegenerative disorders [9]. Much of early development of 8-HQ chelates was related to their use as a precipitant for metal ions, such as aluminium(III), in gravimetric analysis [10-12]. With the demise of standard gravimetric analysis for analytical applications, these applications are mainly of historical interest. However, the excellent chemical, spectral and optoelectronic properties of these complexes led to their development for a wide range of other applications, many of which depend on their fluorescence. Of major importance is the observation at Kodak of electroluminescence from tris(8-hydroxyquinoline)aluminium (III) (Alq_3) [6] has led to its use in organic light emitting devices for a wide variety of display applications. It has been shown that the efficiency of these can be dramatically enhanced by incorporation of phosphorescent heavy metal complexes [13], which allow the capture of electronic excitation energy from both the excited singlet and triplet states of Alq_3 [14]. The luminescence of complexes of 8-HQ also provides a sensitive analytical technique for the detection and quantification of metal ions [15-17], and can lead to selective metal ion determination by use of time resolved measurements [18]. This can be extended through rational design, such as the development of 8-

hydroxyquinolates linked to fluorene based conjugated polymers to produce highly sensitive and selective sensor arrays for a wide variety of metal cations [19]. The 8-hydroxyquinolate ligand also finds use as a selective sorbent of toxic metals [20], and it is of interest to combine the analytical and absorption applications in areas such as surface water remediation.

The unsubstituted 8-HQ is only poorly soluble in water. However, water soluble 8-HQ derivatives, such as 8-hydroxyquinoline-5-sulfonic acid (sulfoxine, 8-HQS), are commercially available. These permit both sensing in aqueous solutions, and concentration of the metal ions under environmental conditions. Marked increases in 8-HQS fluorescence are seen on complexation, and these can be used as turn-on fluorescence sensors [21]. Fluorescence quantum yields are relatively modest in aqueous solutions. However, they can be dramatically enhanced by use of solid polymeric supports [22], providing possibilities of developing sensors for metal ions in surface waters. However, although a number of reports have been presented on spectral and photophysical properties of 8-HQS in the presence of a wide variety of metal ions [21], detailed structural information is still lacking. This is important for the rational design of both fluorescence sensors and systems for concentration of heavy metal ions from aqueous solutions. We have recently applied a combination of multinuclear NMR spectroscopy, DFT calculations and luminescence techniques to provide a picture of what happens when 8-HQS interacts with Zn(II) in water [23]. Multinuclear NMR has been shown to be an excellent method for unraveling the complex equilibria present in solutions of metal ions and organic ligands [24,25], while the application of DFT calculations to simulate multinuclear NMR spectra provides detailed insights into structures of metal complexes in solution [26,27]. The studies with Zn(II) and 8-HQS showed the formation of a single complex with 1:2 (metal:ligand) stoichiometry having a square bipyramidal geometry, with the two 8-HQS ligands and metal in the same plane, and two coordinated water molecules mutually *trans*. The theoretical calculations provide hints that this behavior may strongly depend on the metal ion, and we extend these studies by applying a similar methodology to the complexes of Cd(II) and Hg(II) with 8-HQS. A comparative study is presented of the complexation of the divalent cations of group 12 metals with this ligand in aqueous solution.

2. Experimental

Materials

Analytical grade cadmium(II) nitrate tetrahydrate, mercury(II) sulfate and 8-hydroxyquinoline-5-sulfonic acid hydrate were used as received. Some preliminary studies used mercury(II) chloride, but it was found that chloride competed with 8-HQS in the complexation reaction. For the NMR studies, the solutions were prepared in D₂O (99.9%, Aldrich) and the pH was adjusted (cautiously, to reduce the possibility of drastic local disturbances of equilibria that may be slow to disappear) by addition of DCl and NaOD (Aldrich); the pH* values given are the observed room temperature measurements after standardization with buffers in H₂O solution. Milli-Q water was used for UV/visible absorption and fluorescence studies.

NMR experiments

The ¹H spectra were obtained on a Varian Unity-500 NMR spectrometer (at 499.843 MHz). The methyl signal of *tert*-butyl alcohol was used as internal reference (δ 1.3) relative to TMS.

Computational Details

All the molecular structures were optimized at the DFT level using the GAMESS code [28] employing the B3LYP (Becke three-parameter Lee-Yang-Parr) [29,30] exchange correlation functional. To investigate the coordination mode of Cd²⁺ and Hg²⁺ to HQS, both tetrahedral [M(HQS)₂]²⁻, octahedral *trans*-[M(HQS)₂(H₂O)₂]²⁻ and octahedral *cis*-[M(HQS)₂(H₂O)₂]²⁻ (M=Cd²⁺, Hg²⁺) structures were optimized using the LanL2TZ [31-33] valence and effective core potential (ECP) functions for the metals and the 6-31G(d,p) basis sets for the ligand atoms. The tetrahedral and the *cis*-[M(HQS)₂(H₂O)₂]²⁻ structures were built imposing a C₂ symmetry and the *trans*-[M(HQS)₂(H₂O)₂]²⁻ structure has a C_i symmetry. The structures were optimized considering the bulk solvent (water) effects through the polarizable continuum model (PCM) [34,35]. Default van der Waals radii were used for all atoms except cadmium and mercury, for which 2.96 Å and 2.98 were used, respectively. The Hessian was calculated for the resultant stationary points, and all were characterized as true minima (i.e., no imaginary frequencies). In all cases, the gradient threshold for geometry optimization was taken as 10⁻⁵ hartree bohr⁻¹.

The hydration of the four coordinated tetrahedral and square-planar geometries of $[M(\text{HQS})_2]^{2-}$ with two water molecules was investigated using the same basis sets and ECP referred above (the solvent effects were included using the PCM).

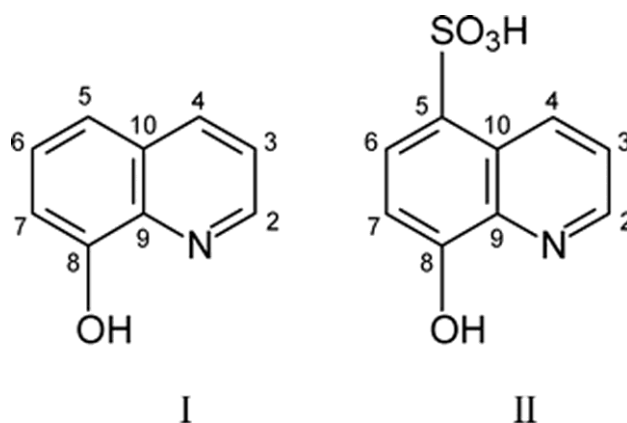
Photophysical studies

UV/visible absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3-22 spectrometers, respectively. Fluorescence spectra were registered with excitation at 330 nm and were corrected for the wavelength response of the system. When not being used for measurements, all samples were kept in the absence of light. Fluorescence quantum yields were measured using quinine sulfate in 0.5 M sulfuric acid ($\Phi_F= 0.55$) [36] and quaterthiophene in acetonitrile ($\Phi_F= 0.16$) [37] as standards.

Flash photolysis experiments were performed with an Applied Photophysics laser flash photolysis equipment pumped by the third harmonic (355 nm) of a Nd:YAG laser (Spectra Physics). Signals were detected with Hamamatsu IP28 and R928 photomultipliers and transient spectra were obtained by monitoring the optical density change at 20 nm intervals over the 440-600 nm range, averaging at least 10 decays at each wavelength. Further details have been given elsewhere [38]. The triplet formation quantum yield (Φ_T) was obtained by comparing the initial absorbance of an optically matched solution (at the laser wavelength) of the 1:2 (metal:ligand) complex [39], with that of a solution of benzophenone in benzene as actinometer ($\epsilon_T = 7630 \text{ M}^{-1} \text{ cm}^{-1}$, and $\Phi_T= 1.00$) [40]. Attempts were made to determine the sensitized singlet oxygen ($^1\Delta_g$) yields by direct measurement of the phosphorescence at 1270 nm following irradiation of an aerated solution of the 1:2 (metal:ligand) complex with a frequency tripled pulse (355 nm) from a Nd:YAG laser, in a system described in detail elsewhere [38]. However, signals were very weak and it was not possible to obtain any quantitative information, in agreement with the low triplet quantum yields determined by flash photolysis.

3. Results and Discussion

Schemes I and II show the structures of 8-hydroxyquinoline (8-HQ) and the water soluble derivative 8-hydroxyquinoline-5-sulfonic acid (8-HQS).



Both 8-HQ and 8-HQS are well-known bidentate chelating agents, able to form extremely stable complexes with most transition and main group metal cations. The proton and carbon chemical shifts, as well as the proton-proton coupling constants of 8-HQS have been measured, in aqueous solution over the whole pH range, and completely assigned in a previous study [23]. The ^1H and ^{13}C NMR chemical shifts were found to change with pH, indicating differences in the degree of protonation/deprotonation of the various acidic functions present in the molecule, whilst the proton-proton coupling constants shows no significant changes. This indicates that there are no significant conformational changes, such as would be expected for any keto-enol tautomerism.

We extend our previous study of the complexation of Zn^{2+} with 8-HQS [23] to the systems Cd(II) and Hg(II)/8-HQS. In aqueous solution over the pH range 5.0–8.5, all of the mixtures of cadmium nitrate and mercury sulphate and 8-HQS show one set of ^1H signals, broadened and/or shifted relative to the free ligand under the same conditions. These are attributed to the presence of complexed forms of 8-HQS in fast exchange with the free ligand. Figure 1 show the ^1H NMR spectra of 8-HQS alone and in the presence of Cd^{2+} and Hg^{2+} ions. For comparison, the ^1H NMR spectrum of 8-HQS in the presence of Zn^{2+} ions is also included. Parallel studies on the complexation between 8-HQS and each of the metal ions were carried out using UV-Visible absorption and fluorescence spectroscopy. Upon addition of Cd(II) or Hg(II) there are changes in the absorption and fluorescence spectra. In particular, the fluorescence intensity of 8-HQS increases upon complexation with the metal. Studies using Job's method in both UV/visible absorption and fluorescence spectra show the stoichiometry 1:2 (metal:ligand) for the dominant

species, for both of the systems. Typical data for Cd(II) are shown in Figure 2. Species with other stoichiometries may be present at low concentrations, and a local maximum in the Job plot around 0.5 also suggests the possibility of the presence of a 1:1 species. Previous reports on the complexation of Cd(II) with 8-HQS has suggested formation of 1:1 and 1:2 complexes, but indicate that only the 1:2 complex is fluorescent [41]. In the NMR spectra, proton chemical shifts of the aromatic ligands provide a good indication of the chelation sites of the ligand upon complexation. Inductive effects at specific positions in the aromatic rings allow the identification of the electronic environment of the coordination site [42]. For 8-HQS, changes in the chemical shifts for the ring protons upon chelation provide insights into the nature of the metal–ligand bonds and the structure of the chelate species, in particular the symmetry of the coordinated ligands. As can be seen in Figure 1, the ^1H NMR spectra, for each of the systems, show only one set of five broad signals, which suggests that free and complexed ligands are in fast exchange. Only the protons H-7 and H-2, which are adjacent to the coordination sites, undergo significant broadening and change in the chemical shift (to low frequency) on complexation (Figure 1 and Table 1). This observation supports the involvement of deprotonated quinoline nitrogen and hydroxyl (O⁻) groups in the complexation [23]. The detection of only one set of signals in the ^1H NMR spectra for the mixtures of metal ions/8-HQS means that equivalent nuclei in the complexed ligand moieties are magnetically equivalent (*i.e.* they have the same chemical shift), indicating that in the 1:2 (metal:ligand) complex, suggested by the Job's plot, the two ligand molecules are magnetically equivalent. The presence of additional minor contributions cannot be ruled out, as the free and complexed ligands are in fast exchange. In addition, ^1H NMR spectra suggest that the stability of complexed species follows the order $\text{Zn}(\text{8-HQS})_2 \leq \text{Cd}(\text{8-HQS})_2 > \text{Hg}(\text{8-HQS})_2$, according to the coordination induced shifts ($\Delta\delta$) for H-2 and H-7. Previous results from potentiometric titrations suggested that the second formation constant for the zinc(II) complex is slightly greater than that with cadmium(II) [43]. However, the values are strongly dependent upon ionic strength, and the authors indicated significant uncertainties in the second stability constants (*i.e.* for formation of the 1:2 species). Further, the same authors reported that the solubility product of the cadmium(II) and zinc(II) species are comparable [44].

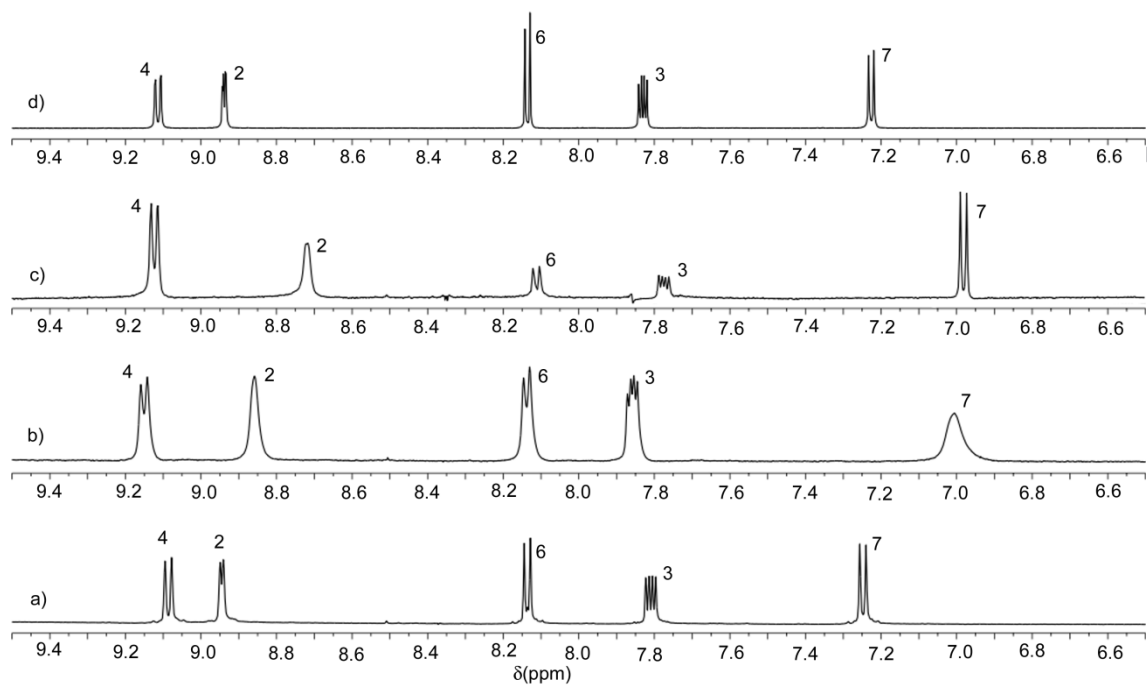


Figure 1. ¹H NMR spectra (499.824 MHz) of D₂O solutions of a) 8-HQS 10 mmol dm⁻³, pH* 7.0, b) Zn(II)/8-HQS 5:10 mmol dm⁻³, pH* 7.5, c) Cd(II)/8-HQS 5:10 mmol dm⁻³, pH* 7.2 and d) Hg(II)/8-HQS 5:10 mmol dm⁻³ pH* 6.5, temperature 298 K.

Table 1. ^1H NMR parameters ^a for 8-HQS and its complexes with Zn(II), Cd(II) and Hg(II) (298K).

	H-2	H-3	H-4	H-6	H-7	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{6,7}$
8-HQS ^b									
pH*=7.0	8.95	7.81	9.09	8.14	7.25	4.2	8.7	1.0	8.2
Zn(II)/8-HQS ^c									
complex a (pH* 7.5)									
δ	8.86	7.86	9.15	8.13	7.01	4.5	8.6	- ^d	8.2
$\Delta\delta$	-0.09	0.05	0.06	-0.01	-0.24				
Cd(II)/8-HQS ^e									
complex a (pH* 7.2)									
δ	8.72	7.78	9.12	8.11	6.98	4.4	8.7	- ^d	8.2
$\Delta\delta$	-0.23	-0.03	0.03	-0.03	-0.27				
Hg(II)/8-HQS ^f									
complex a (pH* 6.5)									
δ	8.94	7.83	9.11	8.14	7.21	4.4	8.7	- ^d	8.2
$\Delta\delta$	-0.01	0.02	0.02	0.00	-0.04				

^a δ values, in ppm, relative to Me_4Si , using *tert*-butyl alcohol ($\delta_{\text{H}}=1.3$) as internal reference; J values in Hz.

^b 10 mmol dm^{-3} 8-HQS solution.

^c 5:10 mmol dm^{-3} Zn(II)/8-HQS solution.

^d not detected.

^e 5:10 mmol dm^{-3} Cd(II)/8-HQS solution.

^f 5:10 mmol dm^{-3} Hg(II)/8-HQS solution.

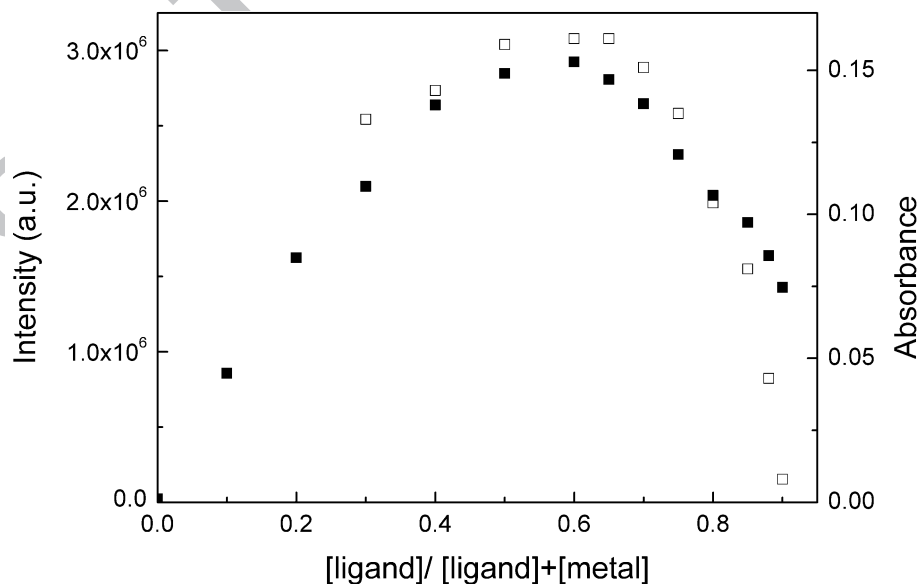


Figure 2. Job's plot based on photophysical studies (\square absorbance and \blacksquare fluorescence intensity) for the system Cd(II)/8-HQS (total concentration of complexing species $1 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6, temperature 298 K).

To help elucidate the coordination mode of Cd^{2+} and Hg^{2+} with HQS in solution theoretically, we have considered the three most important possible geometries: a tetrahedral geometry for the $[\text{M}(\text{HQS})_2]^{2-}$ ($\text{M} = \text{Cd}^{2+}, \text{Hg}^{2+}$) complex and the *cis* and *trans* isomers of the octahedral $[\text{M}(\text{HQS})_2(\text{H}_2\text{O})_2]^{2-}$ structure. The geometries were optimized at the DFT level and minima were found both for the tetrahedral and the octahedral geometries, leaving some ambiguity concerning the coordination number of the metal centres. The next step consisted of carrying out a computation where the hydration with two water molecules of previously optimized tetrahedral and square planar geometries of $[\text{M}(\text{HQS})_2]^{2-}$ was analyzed. To accomplish this, two (non-bonded) water molecules were placed at 2.8 Å in the cadmium structures above and below the metal atom, with the oxygen atoms oriented towards the metal. For the mercury(II) structures, the two water molecules were placed at 3.0 Å. The geometries were subsequently optimized at the DFT level under PCM (water) conditions and it was found that in all the cases the two water ligands readily coordinate to the metals, affording hexacoordinated metal centres. Therefore, the results point to a preference for a six-coordinated sphere, both for the $\text{Cd}^{2+}/8\text{-HQS}$ and the $\text{Hg}^{2+}/8\text{-HQS}$ complexes in aqueous solution. This is in agreement with what we have found with zinc(II) and 8-HQS in water [23]. We have then considered the two possible isomers for the octahedral structure, the *cis* and the *trans* isomers (with respect to the coordinated water molecules). The energies of the isomers were compared and, interestingly, in contrast to what was found for the $\text{Zn}^{2+}/8\text{-HQS}$ complex [23], the *cis* isomer is more stable than the *trans* isomer for $\text{Cd}^{2+}/8\text{-HQS}$ and $\text{Hg}^{2+}/8\text{-HQS}$ systems. The proposed geometries for the complexes and the corresponding HOMO and LUMO orbitals are shown in Figure 3 (the geometry and frontier orbitals of the Zn complex are also shown for comparison). Figure 4 presents a diagram where the relative energies of the *cis* and *trans* isomers are shown for all three metal systems. This shows an increasing stability of the *cis* isomer relative to the *trans* isomer on descending the periodic group. This may be associated with the increasing soft acid characteristics of the metal ion.

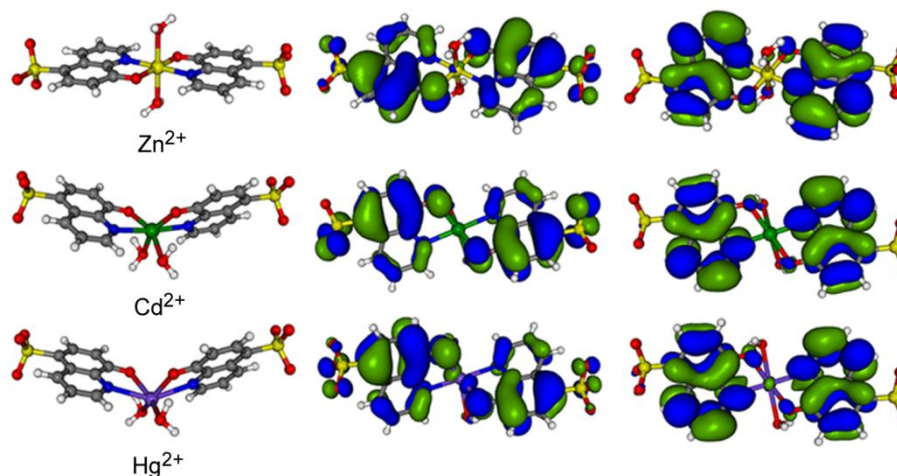


Figure 3. Optimized geometries (left), HOMO (middle) and LUMO (right) of $[\text{Cd}(8\text{-HQS})_2(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Hg}(8\text{-HQS})_2(\text{H}_2\text{O})_2]^{2-}$ calculated at B3LYP/LanL2TZ/6-31G(d,p) level in PCM (water). Calculations for the $[\text{Zn}(8\text{-HQS})_2(\text{H}_2\text{O})_2]^{2-}$ complex [23] were carried out at the B3LYP/ 6-311G(d,p) level in PCM (water).

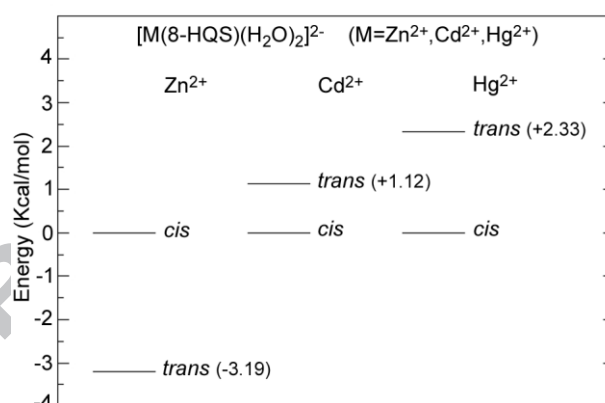
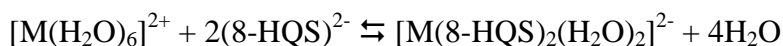


Figure 4. Diagram showing the relative energies of the *cis* and *trans* isomers for the $[\text{M}(8\text{-HQS})_2(\text{H}_2\text{O})_2]^{2-}$ ($\text{M}=\text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$) complexes (in each system the energy of the *cis* isomer was set as zero).

As indicated earlier, the complexation between 8-HQS and Cd(II) and Hg(II) has also been investigated using UV-Vis absorption and fluorescence spectroscopy. Figure 5 shows the absorption and fluorescence spectra of 8-HQS alone and with increasing concentrations of Cd(II) and Hg(II) at pH 6. As the Cd(II) and Hg(II) concentration increases and complexation between 8-HQS and the metals occurs, there is a decrease in absorption of the band with a maximum around 310 nm and the formation of a new

band with an absorption maximum around 365 nm (for Cd(II)) and 385 nm (for Hg(II)) is observed, which corresponds to the allowed $a_g \rightarrow a_u$ transition. An isosbestic point can clearly be seen showing that there is a single equilibrium between two species ($M=Cd^{2+}, Hg^{2+}$), which, based on the Job plots and DFT calculations, we assign to:



As previously reported for Zn(II), upon addition of Cd(II) or Hg(II), the fluorescence intensity of 8-HQS increases as a result of the complexation between the metal and 8-HQS [23]. A shift of the emission maximum to longer wavelengths is observed on complexation with Cd(II). In contrast, with Hg(II), a slight shift to shorter wavelengths is seen, possibly reflecting a weaker binding. Fluorescence quantum yields for the 1:2 (metal:ligand) complex were determined using both quinine sulfate in 0.5 M sulfuric acid ($\Phi_F = 0.55$) [36] and quaterthiophene in acetonitrile ($\Phi_F = 0.16$) [37] as standards. Combining with the previous results for the Zn(II) complex with 8-HQS [33], values of 0.036, 0.052 and 0.005 were obtained for the fluorescence quantum yield for the metal ions Zn(II), Cd(II) and Hg(II), respectively, using quinine sulfate as standard. Slightly lower values were found with quaterthiophene. These results are in agreement with previous reports of an increase in fluorescence quantum yields of the complex of 8-HQ [17] and 8-HQS [21] on going from Zn(II) to Cd(II). Although the complex with Hg(II) has previously been reported to be non-fluorescent [21], we were able to detect weak fluorescence. However, the fluorescence quantum yield of the complex of Hg(II) with 8-HQS is considerably lower than with the other two Group 12 divalent cations, probably due to the heavy atom effect [45]. Incorporation of heavy atoms in 8-hydroxyquinolates has been reported to enhance intersystem crossing due to increased spin-orbit coupling [46], leading to triplet state formation. Attempts were made to study the triplet state of the metal:ligand complexes by flash photolysis. The signals were very weak, but a broad band with a maximum in the same region of the triplet spectra of tris(8-hydroxyquinoline)aluminium(III) (Alq_3) (~ 520 nm) [14] could be observed. Using a solution of benzophenone as standard, the triplet formation quantum yield (Φ_T) was determined as 0.022 and 0.049 for the Zn(II) and Cd(II) complexes, respectively. This supports enhanced intersystem crossing with the heavier Cd(II) complex. However, the sum of fluorescence and triplet quantum yields is very much less than unity, indicating a major competing non-radiative deactivation process of the excited

states. The NMR spectral results suggest that these complexes are relatively labile. We believe that solvent or ligand exchange provides an efficient non-radiative pathway for deactivation of the excited states. This is consistent with the mechanism of solvent thermal quenching reported for related systems [47].

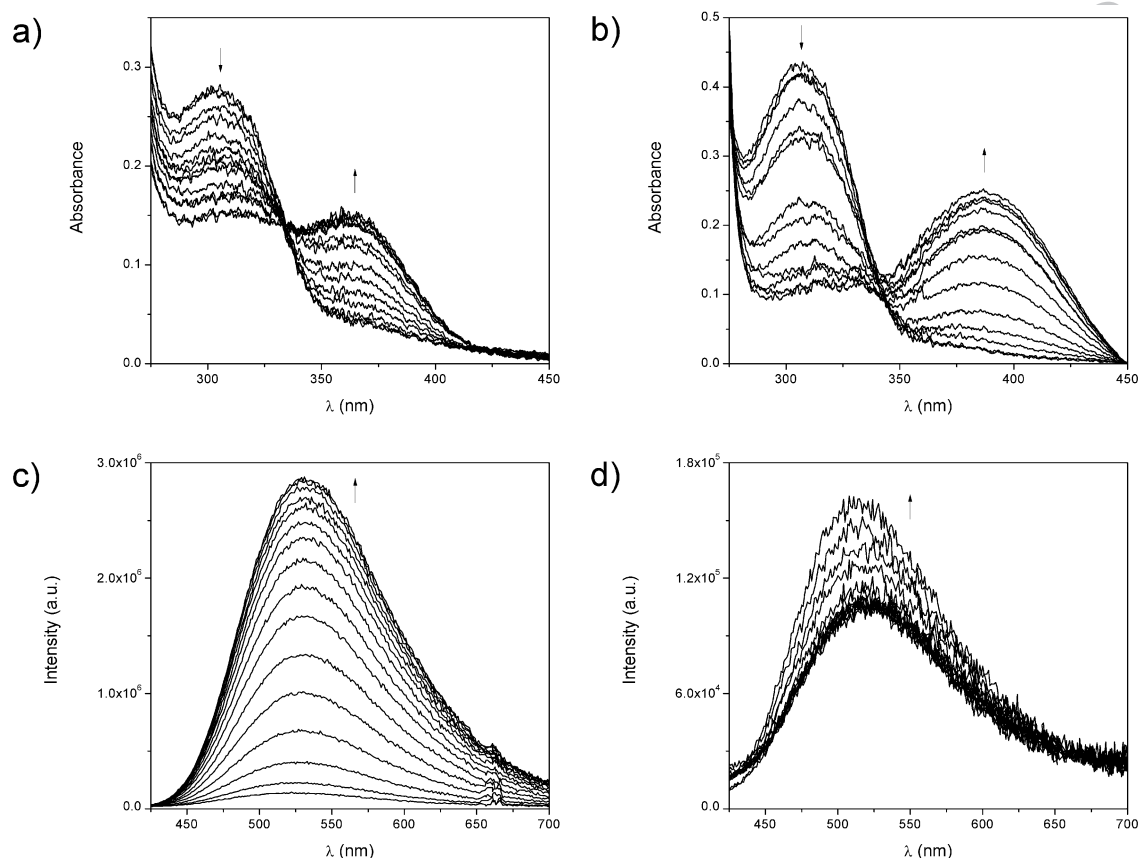


Figure 5. Absorption and fluorescence spectra of 8-HQS (1.0×10^{-4} mol dm $^{-3}$) alone and in the presence of increasing concentrations of Cd(II) ((a) and (c), respectively) and Hg(II) ((b) and (d), respectively) (1.0×10^{-6} – 9.1×10^{-5} mol dm $^{-3}$) for pH 6.

4. Conclusion

We have recently reported a detailed study of the complexation of 8-hydroxy-5-sulfoquinoline (8-HQS) with Zn(II) [23]. We have extended these studies to Cd(II) and Hg(II), using ^1H NMR spectroscopy, DFT calculations and luminescence techniques, to provide detailed information on these complexes for the whole series of Group 12 divalent metal ions. DFT results suggest that the ligand geometry around the metal centre is highly dependent on the hard/soft properties of the metal. The 1:2 (metal:ligand) complex of Zn^{2+} with 8-HQS is square bipyramidal, with the two

coordinated water molecules mutually *trans*, and the remaining positions occupied by the donor groups of the two coordinated 8-HQS ligands [23]. The corresponding 1:2 complexes of Cd^{2+} and Hg^{2+} with 8-HQS show an increasing distortion of the positions of the two water molecules around the metal centre. Along the group 12, there is a pronounced tendency of the two water molecules to adopt mutually *cis* positions, which we believe to be related to the increasing soft acid properties of the metal. Complexation is accompanied by marked changes in the UV/visible absorption and fluorescence spectra, in line with previous studies. In addition, 8-HQS shows a marked increase in the intensity of the fluorescence band compared to the fluorescence of the free ligand on binding to metal ions. However, the fluorescence quantum yields follow the order $\text{Zn}/8\text{-HQS} < \text{Cd}/8\text{-HQS} > \text{Hg}/8\text{-HQS}$. The increase in quantum yield on going from Zn(II) to Cd(II), which is in agreement with previous studies [21], and also with the NMR results on the complex stability, and may well be associated with the changes from dominant *trans* to *cis* geometrical isomer. With the zinc(II) and Cd(II) systems, the sum of fluorescence and triplet state quantum yields is very much less than one, suggesting a competing non-radiative pathway. We believe that this involves solvent exchange. Development of fluorescence sensors of these metal ions based on 8-HQS is likely to benefit from minimizing solvent exchange through immobilization in solid supports, such as ion-exchange resins [22] or intercalated double hydroxides [48]. These observed changes are likely to be particularly important for the potential application of 8-HQS as a luminescent sensor for the detection and remediation of Zn(II), Cd(II) and Hg(II) in surface waters and biological fluids. In addition they may be useful for applications in organic light emitting diodes (OLEDs).

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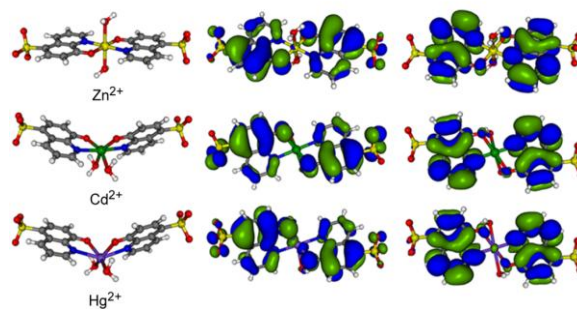
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Theoretical and experimental insights into the complexation of 8-hydroxyquinoline-5-sulfonate with divalent ions of Group 12 metals^r

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Graphical Abstract



Highlights

- Zn(II), Cd(II) and Hg(II) form dominant 2:1 complexes with 8-hydroxyquinoline-5-sulfonate (8-HQS)
- These all have hexacoordinated metal centres, with two 8-HQS and two water molecules
- However, while the Zn(II) complex has water molecules in the *trans* configuration, the *cis* isomer is more stable with Cd(II) and Hg(II)