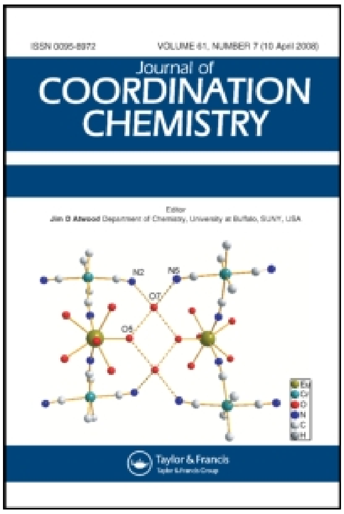

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Synthesis, characterization and fluorescence spectra of mononuclear Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand

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Synthesis, characterization and fluorescence spectra of mononuclear Zn(II), Cd(II) and Hg(II) complexes with 1,10-phenanthroline-5,6-dione ligand

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The mononuclear complexes of Zn(II), Cd(II) and Hg(II), [Zn(phen-dione)Cl_2], [Cd(phen-dione)Cl_2] and [Hg(phen-dione)Cl_2], where phen-dione = 1,10-phenanthroline-5,6-dione, have been synthesized and characterized by elemental analysis and IR, ^{1}H NMR and electronic absorption spectroscopies. The ν(C=O) of coordinated phen-dione ligands in these complexes shows that the phen-dione is not coordinated to metal ion from its C=O sites. Electronic spectra of the complexes show two absorption bands for intraligand transitions. These absorption bands show dependence on the dielectric constant of solvents. These complexes exhibit an intense fluorescence band around 545 nm in DMSO when the excitation wavelengths are 200 nm at room temperature.

Keywords: 1,10-Phenanthroline-5,6-dione; Zinc; Cadmium; Mercury; Metal to ligand charge transfer; Fluorescence

1. Introduction

1,10-Phenanthroline (phen) and some of its derivatives such as 5,6-diamino-1,10-phenanthroline (phen-diamine), 1,10-phenanthroline-5,6-dione(phen-dione) and 1,10-phenanthroline-5,6-dioxime (phen-dioxime) play important roles as molecular scaffolds for supramolecular assemblies and ligands for synthesis of ring-opening metathesis polymerization (ROMP) monomer [1–4]. Especially important and desirable derivatives are those which retain twofold symmetry of this ligand and thereby avoid some of the stereochemical problems associated with their *tris* chelated metal complexes, namely formation of *mer* and *fac* isomers. 5,6-Diamino-1,10- phenanthroline (phen-diamine) is particularly important in that it can either directly bridge two metal centers or be condensed with a variety of ortho-quinones to form addition derivatives. For example, the useful bridging ligand, tetrapyrido[3,2-a:2′,3″,2″-h:2‴,3‴-j]phenazine (tpphz),

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is readily formed upon condensation of phen-diamine with 1,10-phenanthroline-5,6-dione(phen-dione) [3–5].

The focus of this manuscript is on complexes of 1,10-phenanthroline-5,6-dione (phen-dione) because this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an *o*-quinone moiety with pH-dependent electro activity [6–7]. Metal complexes of this ligand potentially allow for variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes [8].

Metal complexes of the type $[M(LL)_3]^{n+}$, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [9]. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing access to understanding of details involved in DNA-binding and cleavage [10–11]. Clearly, further studies using various phen-dione complexes such as $[M(\text{phen-dione})_3]^{n+}$, $[M(\text{phen-dione})_2\text{tpphz}]^{n+}$ and $[M(\text{phen-dione})_2(LL')]^{n+}$ are needed to evaluate the influence of metal-ion-induced geometry, charge, spin-state, redox potential, etc. changes on the DNA binding and cleavage mechanisms in this important class of complexes as was the case with the previously reported metalloderivatives ($M = Ru^{II}$, Rh^{III}, Co^{III}, Cr^{III}, etc.) of phen or modified phen ligands [9–15]. We now report the preparation, characterization and fluorescence spectral measurement of $[Zn(\text{phen-dione})Cl_2]$, $[Cd(\text{phen-dione})Cl_2]$ and $[Hg(\text{phen-dione})Cl_2]$.

2. Experimental

2.1. *Materials and measurements*

All chemicals and solvents were reagent grade, obtained from either Merck or Aldrich and used without further purification. 1,10-Phenanthroline-5,6-dione (phen-dione) was synthesized according to the literature procedure [16].

Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (4000–400 cm^{-1}) were measured on a FT-IR JASCO 460 spectrophotometer with KBr pellets and electronic spectra on a JASCO 7850 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DRX-500 MHz, AVANCE spectrometer at ambient temperature in DMSO-d_6. Fluoresence measurements were made on a Cary Eclipse Fluoresence spectrophotometer equipped with quartz cuvettes of 1 cm path length.

2.2. *Synthesis of [Zn(phen-dione)Cl$_2$]*

The phen-dione (0.210 g, 1 mmol) was dissolved in 30 cm^3 ethanol and added drop-wise to the solution of $ZnCl_2$ (0.136 g, 1 mmol) in 30 cm^3 ethanol and stirred and heated at 40°C for 20 h. The yellow precipitate was collected by suction filtration and washed with ethanol and ether, yield: 0.29 g (85%), giving a satisfactory elemental analysis: Anal. Calcd for $ZnC_{12}H_6N_2Cl_2O_2$: C, 41.56; H, 1.74; N, 8.08; Zn, 18.87%. Found: C, 41.90; H, 1.81; N, 8.24; Zn, 18.78%.

2.3. *Synthesis of [Cd(phen-dione)Cl$_2$]*

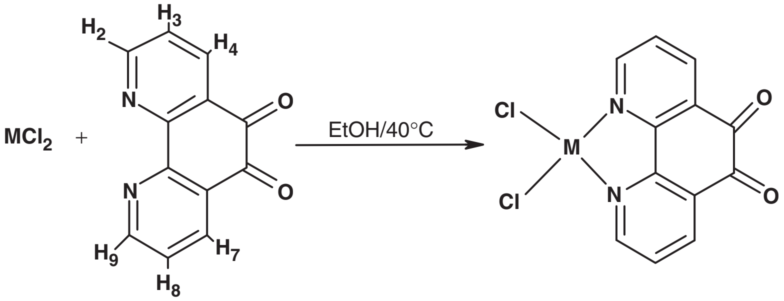
This complex was prepared by following the same procedure described for [Zn(phen-dione)Cl$_2$]. The light yellow precipitate was collected. Yield: 0.32 g (81%). Anal. Calcd for $CdC_{12}H_6N_2Cl_2O_2$: C, 36.68; H, 1.63; N, 7.05; Cd, 28.56%. Found: C, 36.66; H, 1.70; N, 7.12; Cd, 28.49%.

2.4. *Synthesis of [Hg(phen-dione)Cl$_2$]*

This complex was prepared by following the same procedure described for [Zn(phen-dione)Cl$_2$]. The product was pale yellow. Yield: 0.36 g (80%). Anal. Calcd for $HgC_{12}H_6N_2Cl_2O_2$: C, 29.89; H, 1.25; N, 5.81; Hg, 41.64%. Found: C, 29.95; H, 1.31; N, 5.88; Hg, 41.50%.

3. Results and discussion

These complexes were synthesized in good yield according to the following reaction (scheme 1):



Scheme 1. Reaction pathway for the synthesis of the complexes (M = Zn^{2+}, Cd^{2+} and Hg^{2+}).

Under these conditions, the phen-dione preferentially binds to M^{II} through the nitrogen instead of the carbonyl groups attributable to the different bite angles of the *oxy-* *versus* *azo*-sites with the current metals preferring the *azo*-site. This is similar to previous studies of Cu^{2+}, Co^{3+}, Co^{2+}, Ru^{2+} and Ni^{2+} complexes with phen-dione showing that the phen-dione coordinates to metal ions through their nitrogen atoms [17–21].

The ^{1}H NMR spectral data for the ligand and the complexes show three signals at 7.8–9.2 ppm. These signals arise from the hydrogen atoms of the phen-dione ligand. These hydrogen atoms are labeled as shown in scheme 1 and the data are collected and assigned in table 1. The signals arising from H$_{2,9}$ changed from a doublet of doublets in the ligand to a doublet in the complexes. The relative intensities of these signals are in accord with the proposed structure.

Table 1. ^{1}H NMR spectral data for ligand and [M(phen-dione)Cl_2].[a]

Compound	$H_{2,9}$	$H_{3,8}$	$H_{4,7}$
Ligand	8.5(dd)[b]	7.6(q)[c]	9.1(dd)
[Zn(phen-dione)Cl_2]	8.6(d)[d]	7.7(q)	9.0(dd)
[Cd(phen-dione)Cl_2]	8.6(d)	7.7(q)	9.1(dd)
[Hg(phen-dione)Cl_2]	8.5(d)	7.7(q)	9.1(dd)

[a] In DMSO-d_6, data in ppm *vs.* TMS reference at 0.00 ppm at ambient temperature; [b] Doublet of doublet; [c] Quartet; [d] Doublet.

Table 2. IR data for ligand and [M(phen-dione)Cl_2].[a]

Compound	ν(C=O)	ν(C=N)
Ligand	1685	1556
[Zn(phen-dione)Cl_2]	1695	1584
[Cd(phen-dione)Cl_2]	1688	1580
[Hg(phen-dione)Cl_2]	1692	1578

[a] IR data (KBr pellets) in cm^{-1}; strong absorptions.

The IR spectrum of phen-dione exhibits a band at 1685 cm^{-1} which can be assigned to the C=O stretching vibration. The IR spectra of the complexes exhibit a strong band around 1690 cm^{-1} that is not significantly shifted compared to the spectrum of the uncoordinated ligand. This clearly shows that the ligand is not coordinated from its C=O sites [6–8]. An IR absorption band around 1560 can be assigned to ν(C=N) of the phen-dione ligand. This band is shifted when the phen-dione ligand is coordinated to the metal. The IR spectral data of the ligand and complexes are given in table 2.

In complexes where the phen-dione ligands coordinated to metal ions via C=O moieties such as Ti(O,O′-phen-dione)$_3$, V(O,O′-phen-dione)$_3$, V(O,O′-phen-dione)$_3$($TiCl_4$)$_3$ and Ti(O,O′-phen-dione)$_3$ ($TiCp_2$)$_3$ the ν(C=O) shifted about 200–300 cm^{-1} to lower wave number [22–24].

Electronic spectra of these complexes were taken in DMF. Figure 1 shows the UV-Vis spectrum of [Zn(phen-dione)Cl_2] in DMF.

The absorption bands in the UV region are assigned to ligand-centered $\pi \rightarrow \pi^*$ transitions. However, given that there are different metal ions involved, the similar absorption bands and intensities in spectra of all three complexes imply a similar origin- and one that does not involve metal orbitals. Therefore the intense absorption bands centered at approximately 460 nm are intraligand transitions. These absorption bands are assigned to $n \rightarrow \pi^*$ of the carbonyl group of phen-dione because these bands are shifted toward shorter wavelengths (blue shift) in high dielectric solvents while a red shift was observed for $\pi \rightarrow \pi^*$ transitions in high dielectric solvents [25]. Electronic spectral data for the three complexes in DMF are given in table 3.

Fluorescence emission spectra of the complexes were taken in DMSO with excitation wavelength of 200 nm at room temperature. The fluorescence emission

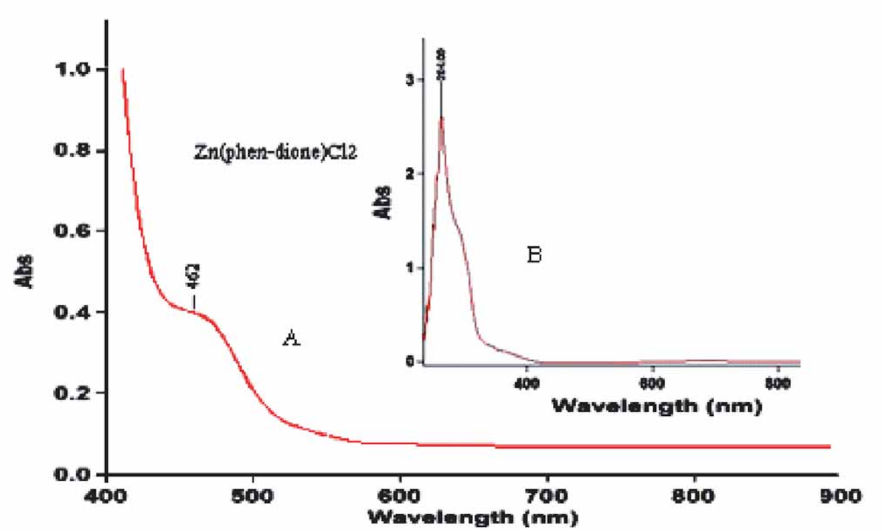


Figure 1. Electronic spectra of (a) [Zn(phen-dione)Cl_2] (1×10^{-3} M) in DMF, (b) [Zn(phen-dione)Cl_2] (1×10^{-4} M) in DMF.

Table 3. UV-Vis data for [M(phen-dione)Cl_2].

Complex	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
[Zn(phen-dione)Cl_2]	264(4.44)	462(2.6)
[Cd(phen-dione)Cl_2]	263(3.92)	458(2.68)
[Hg(phen-dione)Cl_2]	264(4.54)	470(2.52)

$^a\lambda$ in the nm (log ε); in DMF solution.

spectrum of [Zn(phen-dione)Cl_2] is depicted in figure 2. [Cd(phen-dione)Cl_2] and [Hg(phen-dione)Cl_2] exhibit very similar fluorescence spectra. The peaks around 545 nm for all complexes may be attributed to the intraligand emission ($\pi \rightarrow \pi^*$) from the phen-dione [25]. The free phen-dione molecule displays a weak luminescence at ca 543.9 nm. The fluorescence intensity of these complexes is larger than that of the free ligand, probably due to the rigidity of the coordinated ligand in these complexes in comparison to the free ligand. On the other hand, the fluorescence intensity enhancement may be due to coordination of free ligand to M(II) (M = Zn, Cd and Hg) reducing the non-radiative decay of the intraligand excited state [26–27].

The present work describes the reactivity of the metals of group XII with phen-dione. The spectroscopic data for these complexes clearly suggests that the phen-dione ligand is coordinated to metal ions from its C=N moieties. UV-Vis spectroscopy shows two intraligand transition (($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$)). The presence of the free C=O moiety in these complexes has prompted us to study the synthesis of polynuclear complexes and the study of their spectroelectrochemical properties.

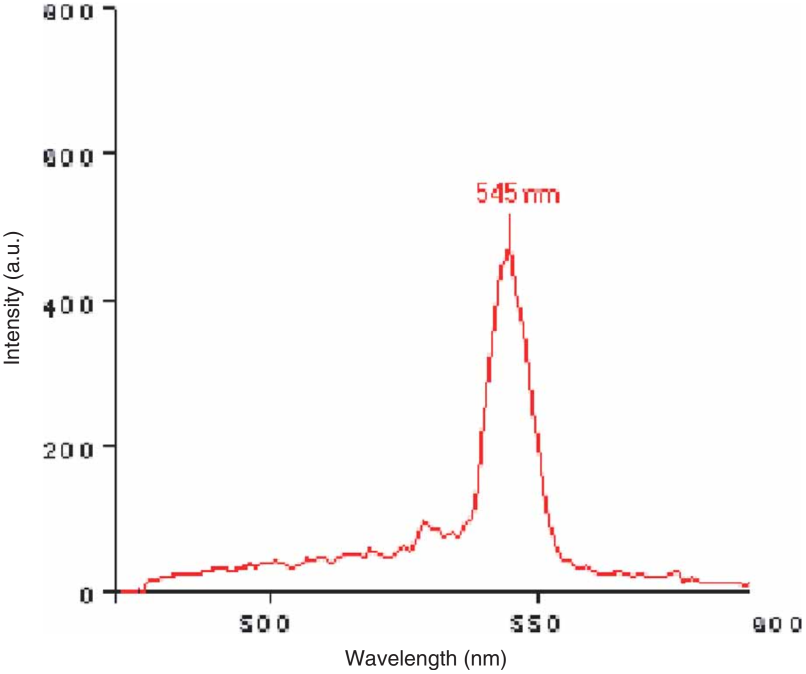


Figure 2. Fluorescence spectrum of [Zn(phen-dione)Cl_2] with ex = 200 nm at room temperature in DMSO.

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