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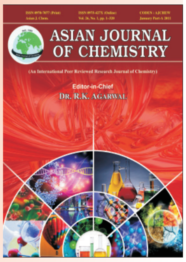

Synthesis, Crystal Structure and Luminescence Properties of Cd(II)-1,10-Phenanthroline Complex

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A new Cd(II) complex, Cd(NO_3)$_2$(Phen)$_2$, was prepared by the reaction of Cd(NO_3)$_2$ with 1,10-phenanthroline in ethanol. The structure of the synthetic Cd(II) complex was determined by single crystal X-ray diffraction analysis and characterized by elemental analysis, molar conductivity and IR spectroscopy. Its fluorescence measurements showed that the Cd(II) complex in solid form has excellent performance on fluorescence emission and the intensity of fluorescence emissions were quenched sharply by solvents, Further, its decreasing intensity seemed to be influenced by the increasing polarity of solvents. The results indicated that the fluorescence intensity of Cd(II) complex quenched dramatically and the quenching efficiency was in the order H_2O > DMF > CH_3OH > CH_3CH_2OH. And the Cd(II) complex can be used as fluorescence sensors toward polarity of solvents.

Keywords: Cd(II) complex, 1,10-Phenanthroline, Synthesis, Crystal structure, Fluorescence property.

INTRODUCTION

Over the past two decades, studies on the organometallic materials have gained considerable attention due to their attractive structures and promising potential applications for catalysis, gas storage, magnetic, luminescence materials[1-7]. Many studies have shown that the organic ligands can coordinate with metal ions in different ways, resulting in the formations of various metal-organic frameworks with specific topologies and useful properties[8,9]. The Cd(II) complexes have gained considerable attention due to their luminescent properties[10]. In this study, we report the synthesis and characterization of a new Cd(II) complex, Cd(NO_3)$_2$(Phen)$_2$. The luminescent properties of the Cd(II) complex in solid form and in solution forms also have been investigated and the results revealed that Cd(II) complex in solid form has excellent fluorescent emission. The effect of solvents on fluorescent intensity and the results indicated the fluorescent intensity of Cd(II) complex quenched dramatically, with the quenching efficiency of H_2O being the highest.

EXPERIMENTAL

All chemicals were obtained from commercial sources and were used without further purification. Elemental analyses (C, H and N) were carried out on a Elementar Vario EL III elemental analyzer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000-400 cm^{-1} region. The molar conductance values was determined on a DDS-11A conductivity meter with methanol as solvent (10^{-3} mol L^{-1} solution) at 25 °C. The luminescent spectrum were performed on a PE LS-55 fluorescence spectrophotometer.

Synthesis of Cd(NO_3)$_2$(Phen)$_2$: The 2 mmol (0.3964 g) of 1,10-phenanthroline was added to the 5 mL of CH_3CH_2OH solution. After being dissolved, 1 mmol (0.3085 g) of Cd(NO_3)$_2$·4H_2O was added to the solution. The mixture was continuously stirred for 2 h at refluxing temperature and then cooled to room temperature. The precipitate was collected by filtration. Yield 61 %. Anal. Calcd. for $C_{24}H_{16}N_6O_6Cd$: C, 48.32; H, 2.68; N, 14.09. Found: C, 48.05; H, 2.37; N, 13.99. Lm (s cm^2 mol^{-1}): 8.3. IR (KBr, ν_{max}, cm^{-1}): 1555 (m, C=N), 1493 (ν_1, NO_3^-), 1301(ν_4, NO_3^-), 815 (ν_3, NO_3^-).

X-Ray crystallography: A colourless prism single crystal with dimensions of 0.28 × 0.20 × 0.18 mm was placed on a glass fiber and mounted on a CCD area detector. Diffraction data were collected by ϕ-ω scan mode using a graphite-monochromatic MoK_α radiation (λ = 0.71073 Å) at 298 K. A total of 11005 reflections were collected in the range 3.02-27.48°, of which 2630 were unique (R_{int} = 0.0296) and 2380 were observed with $I > 2\sigma(I)$. The data were corrected for *Lp* factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The structure was solved by direct methods using SHELXL-97[11] and expanded using Fourier techniques. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package[12]. CCDC reference number: 942225. The most relevant crystal data for complex are quoted in Table-1. The relevant bond lengths and bond angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT FOR Cd(II) COMPLEX

Crystal data	
Chemical formula	$C_{24}H_{16}N_6O_6Cd$
Formula weight	596.83
Cell setting, space group	Monoclinic, C2/c
a (Å)	11.6961(11)
b (Å)	15.2386(14)
c (Å)	13.4462(12)
α (°)	90.00
β (°)	106.029(2)
γ (°)	90.00
Volume (Å^3)	2303.4(4)
Z	4
Dc(Mg m^{-3})	1.721
μ (mm^{-1})	1.003
Crystal size (mm)	0.28 × 0.20 × 0.18
Radiation (Å)	Mo Kα, 0.71073
Theta min–max (°)	3.02-27.48
Tot., uniq. data, R(int)	11005, 2630, 0.0296
Observed data [I > 2σ(I)]	2380
F (000)	1192
Goodness-of-fit on F^2	1.072
R_1 [I > 2σ(I)]	0.0300
ωR_2 [I > 2σ(I)]	0.0725
R_1 (all data)	0.0321
ωR_2 (all data)	0.0735
Min. and max. resd. dens. [e/Å^3]	0.971, -0.291
CCDC no.	942225

RESULTS AND DISCUSSION

Properties of the Cd(II) complex: The result of elemental analysis indicated that the composition of Cd(II) complex conforms to a 1:2 metal-to-ligand stoichiometry and is accorded with the result of single crystal X-ray diffraction analysis. The Cd(II) complex is soluble in DMF, DMSO, methanol, a little soluble in ethanol and acetone, insoluble in benzene, diethyl and THF. The molar conductance value of the Cd(II) complex measured in CH_3OH solution (1 × 10^{-3} mol L^{-1}) at 25 °C is 8.3 scm^2 mol^{-1}, showing the Cd(II) complex is non-electrolyte[13].

IR spectra: The IR spectrum of 1,10-phenanthroline ligand shows band at 1589 cm^{-1} and it shifts to 1555 cm^{-1} in the complex, indicating that the nitrogen atoms of 1,10-phenanthroline take part in the coordination with Cd(II) atom. The absorption bands assigned to the coordinated nitrates were observed at 1493 cm^{-1} (ν_{as}) and 815 (ν_s) cm^{-1} for the complex. The separation of the two highest frequency bands $|\nu_1-\nu_4|$ is approximately 200 cm^{-1}, indicating that the coordinated NO_3^- ions in the complex are bidentate ligand[14].

Structural description of Cd(II) complex: The molecular structure of Cd(II) complex is shown in Fig. 1. From Fig. 1, it can be seen that the Cd(II) ion center is eight-coordinated and exhibits a distorted octahedral geometry; Cd(II) ion is coordinated by four N atoms (N1, N2, N1$^{\#1}$, N2$^{\#1}$) belonging to two 1,10-phenanthroline ligands and four O atoms (O1A, O2A, O1A$^{\#1}$, O2A$^{\#1}$), belonging to two nitrates. The Cd-O and Cd-N bond lengths are similar to that reported previously[15]. In the complex, the nitrates adopt bidentate coordinated mode and is in accordance with the result of IR spectrum. The complex molecules form an one-dimensional chained structure that has been created by the π-π stack interaction of 1,10-phenanthroline rings (Fig. 2).

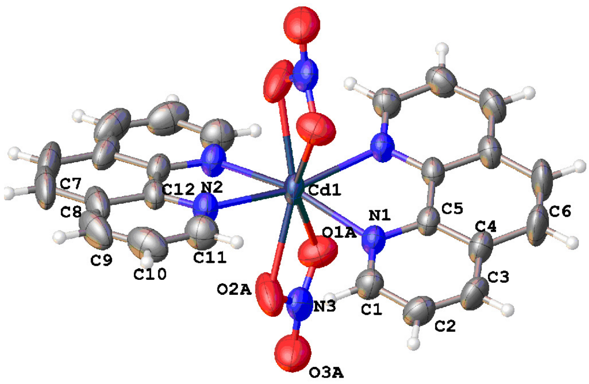

Fig. 1. Molecular structure of Cd(II) complex

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE COMPLEX

Bond length (Å)			
Cd(1)-N(1)	2.3335(15)	Cd(1)-O(1A)	2.492(12)
Cd(1)-N(1)$^{\#1}$	2.3335(15)	Cd(1)-O(1A)$^{\#1}$	2.492(12)
Cd(1)-N(2)	2.3379(17)	C(1)-N(1)	1.328(3)
Cd(1)-N(2)$^{\#1}$	2.3379(17)	C(11)-N(2)	1.324(3)
Cd(1)-O(2A)	2.492(12)		
Cd(1)-O(2A)$^{\#1}$	2.492(12)		
Bond angle (°)			
N(1)-Cd(1)-N(1)$^{\#1}$	72.33(8)	N(1)-Cd(1)-O(2A)	118.6(2)
N(1)-Cd(1)-N(2)	110.11(6)	N(1)$^{\#1}$-Cd(1)-O(2A)	78.7(3)
N(1)$^{\#1}$-Cd(1)-N(2)	165.02(6)	N(1)$^{\#1}$-Cd(1)-O(2A)$^{\#1}$	118.6(2)
N(1)-Cd(1)-N(2)$^{\#1}$	165.02(6)	N(2)-Cd(1)-O(2A)$^{\#1}$	76.1(2)
N(1)$^{\#1}$-Cd(1)-N(2)$^{\#1}$	110.11(6)	N(2)$^{\#1}$-Cd(1)-O(2A)$^{\#1}$	87.5(3)
N(2)$^{\#1}$-Cd(1)-N(2)	71.56(8)	N(2)-Cd(1)-O(2A)	87.5(3)
N(1)-Cd(1)-O(2A)$^{\#1}$	78.7(3)	N(2)$^{\#1}$-Cd(1)-O(2A)	76.1(2)
O(2A)-Cd(1)-O(2A)$^{\#1}$	159.8(6)		

TABLE-3
LUMINESCENT DATA FOR THE Cd(II) COMPLEX

Compound	Solvent	λ_{ex} (nm)	λ_{em} (nm)	RFI[a]
Cd(II) complex	Solid	388	459	255.3
	H_2O	388	449	10.7
	DMF	388	442	25.8
	CH_3OH	388	446	70.3
	CH_3CH_2OH	388	448	104.4

[a]RFI: Relative fluorescence intensity

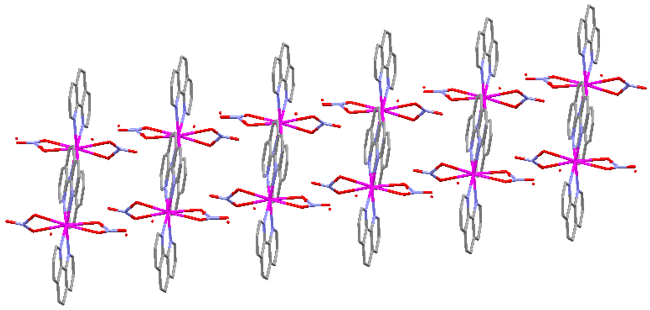

Fig. 2. One-dimension chained structure of Cd(II) complex

Fluorescence properties: The luminescent characteristics of Cd(II) complex in solid form state and in solution forms are listed in Table-3. The emission spectra of the Cd(II) complex in solid form and in solution forms are shown in Fig. 3. From Table-3 and Fig. 3, we can see that the Cd(II) complex shows a maximum emission peak at 459 nm when excited at 388 nm in solid state. The H_2O, DMF, CH_3OH and CH_3CH_2OH solvents can quench the fluorescent intensity. This may be the solvent molecules being partially substituted for the 1,10-phenanthroline ligands in the Cd(II) complex. The quenching effect of solvents for the fluorescence of the Cd(II) complex system is arranged in the order $H_2O > DMF > CH_3OH > CH_3CH_2OH$. The order of fluorescent intensities of the Cd(II) complex system is in agreement with the e values of these solvents. CH_3CH_2OH has the strongest enhancing effect in these organic solvents. The Cd(II) complex can be used as fluorescence sensors toward polarity of solvents.

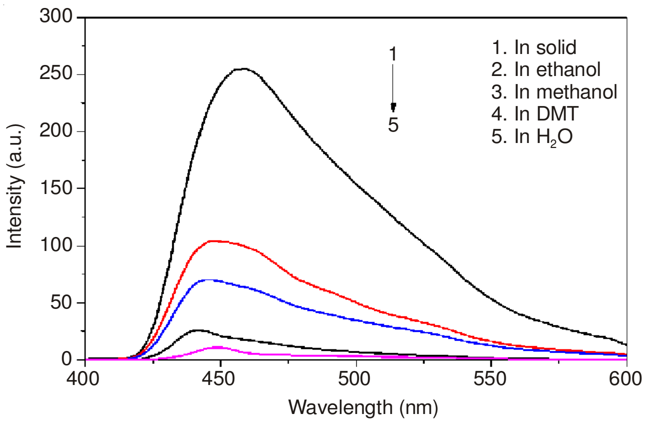

Fig. 3. Emission spectra of Cd(II) complex, The excitation and emission slit widths were 5 nm

Conclusion

The present investigation demonstrated the structure and properties of a new Cd(II) complex. The complex exhibits 1D chained structure, which in solid form has excellent fluorescence emission. The intensity of its fluorescence emissions showed a convincing influence by its solvent environment, as its intensity decreased with increasing the polarity of solvents.

Supplementary material: Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 942225. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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