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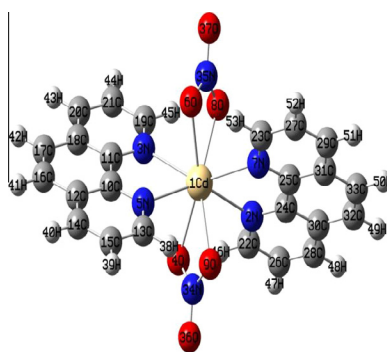
Synthesis, crystal structure, photoluminescence, and DFT studies of bis(1,10-phenanthroline)di(κ^2 OO' nitrate)cadmium(II) [Cd(phen)₂(NO₃)₂]

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HIGHLIGHTS

- A eight coordinated cadmium(II) complex has been synthesized.
- X-ray single-crystal structure analysis and discussion for the complex.
- The complex exhibit photoluminescence properties in solid state.
- The molecular geometry, vibrational frequencies and bonding features have been calculated by DFT.

GRAPHICAL ABSTRACT



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ABSTRACT

A cadmium 1,10-phenanthroline complex, [Cd(phen)₂(NO₃)₂] has been synthesized by and its crystal structure determined. The compound is monoclinic, *C*2/*c*, *a* = 11.5008(2), *b* = 15.3523(2), *c* = 13.2767(2) Å, β = 103.610(2), *Z* = 4. The compound is monomeric with a octacoordinate cadmium ion bonded to two bidentate 1,10-phenanthroline molecules and two bidentate nitrate units. The metal ion is *bis*-chelated by two *N*-heterocycles as well as by two nitrate ions in a distorted dodecahedral CdN₄O₄ coordination environment. The complex is thermally stable up to 110 °C. Photophysical investigation reveals that complex is luminescent in the solid state. The molecular geometry, harmonic vibrational frequencies and bonding features of complex [Cd(phen)₂(NO₃)₂] in the ground-state have been calculated by using the density functional B3LYP method with 3-21G (d, p) as higher basis set. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Finally the calculation results were applied to simulate infrared spectrum of the title compound which show good agreement with observed spectrum.

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Introduction

Divalent ions of group 12 possess complete nd shells and ligand field stabilization has no role in deciding stereochemistry of complex. As a result, the geometries are determined solely by considerations of size and electrostatic or covalent binding forces,

allowing coordination diversity of any accompanying ligand. Despite the lower interest due to their toxic hazards, Cd and Hg complexes seem to be more interesting from a structural point of view because of the ability of these cations to modify both coordination numbers and geometries. As complexes of Cd(II) can assume geometries from tetrahedron, through trigonal bipyramidal, square pyramidal, octahedral to dodecahedron, hence are suitable for development of luminescent coordination complexes. Luminescent properties of monomeric [1–5], multinuclear [6–9] and polymeric [10–14] coordination complexes of Zn(II) and Cd(II) have gained considerable attention. As coordination numbers of cadmium complexes are variable and they exhibit good thermal, chemical and photochemical stability, they can serve as emitter materials with varying optoelectronic properties. 1,10-Phenanthroline has a rigid framework and possesses a superb ability to coordinate many metal ions, which show potential for technological applications, due to their strong absorption in the ultraviolet spectral region, bright light-emission and good electro- and photoactive properties [15–19].

Molecular orbital calculations give a rational understanding of photoluminescence mechanism and have been applied to investigation on mononuclear and multinuclear complexes [20–23]. Reports on structures, photoluminescence, and theoretical studies of Zn(II) and Cd(II) coordination complexes have been reviewed [24]. The possible use of Zn(II) and Cd(II) coordination complexes as electroluminescent materials applied in OLEDs has also been reviewed [25].

In this present study, we report synthesis, crystal structure, photoluminescence, and theoretical studies of a new cadmium complex having unusual distorted dodecahedron geometry.

Experimental and computational

Materials and methods

All materials used for synthesis were of reagent grade and used without further purification. Pyridine-3,5-dicarboxylic acid and 1,10-phenanthroline were purchased from Sigma–Aldrich. Cadmium nitrate hexahydrate was purchased from Acros-Organics and potassium hydroxide from Merck.

Elemental analysis was carried out with a CHNS-932 Leco elemental analyzer. The Fourier Transform Infrared spectra were recorded in the range 4000–400 cm^{-1} on Perkin Elmer – Spectrum RX-IFTIR spectrophotometer with solid KBr pellets. Thermogravimetric analysis was carried out with Mettler Toledo TGA/SDTA 851e in nitrogen atmosphere with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The photoluminescence excitation and emission spectra were measured at room temperature by using Agilent Cary Eclipse Fluorescence Spectrophotometer equipped with a Xenon lamp that was used as an excitation source.

Synthesis of coordination compound $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$

The title compound, $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$, was obtained unexpectedly during an attempt to synthesize a cadmium coordination polymer with complex with pyridine-3,5-dicarboxylic acid as linker and 1,10-phenanthroline as auxiliary ligand. A mixture of pyridine-3,5-dicarboxylic acid (H_2pda ; 0.0334 g, 0.2 mmol) and potassium hydroxide (0.0224 g, 0.4 mmol) were dissolved in minimum amount of distilled water in glass tube. Cadmium nitrate tetrahydrate (0.092 g, 0.3 mmol) was added to the solution and the volume was raised to 6 mL with distilled water. 1,10-Phenanthroline (0.2 mmol, 0.036 g) was dissolved in 5 mL of hot water and was then added to the above reaction mixture. The resulting solution was heated over water bath for 2 h. The glass tube was then

kept for 3 days at room temperature. Colorless crystals of $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ were obtained with yield ~ 0.10 g, 84% based upon 1,10-phenanthroline. Anal. Calcd (%) for $\text{C}_{24}\text{H}_{16}\text{CdN}_6\text{O}_6$: C, 48.30; H, 2.70; N, 14.08. found (%): C, 48.25; H, 2.60; N, 14.17. The crystals were manually selected for structural determination and further characterization.

Single crystal X-ray diffraction structure determination

The structure of the compound $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ was determined by single crystal X-ray diffraction analysis. X-ray intensity data of 7872 reflections (of which 2011 unique) were collected on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The strategy for data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by standard ‘phi-omega’ scan techniques, and were scaled and reduced using CrysAlisPro RED software. The cell dimensions were determined by least-square fit of angular settings of 23,635 reflections in the θ range 2.90–25.00 $^{\circ}$. The intensities were measured by ω scan mode for θ range 2.90–25.00 $^{\circ}$. Data was corrected for Lorentz, polarization factors and absorption effects. The structures were solved by direct methods using SHELXS-97 [26] and refined by full matrix least-squares with SHELXL-97, refining on F^2 [27]. The positions of all the atoms were obtained by direct methods. All non-H-atoms were refined anisotropically. The remaining H-atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 U_{eq} of their parent atoms. The crystal and refinement data are summarized in Table 1 and selected bond distances and bond angles are shown in Table 2.

Computational details

Density functional theoretical (DFT) computations have been performed at the B3LYP/3-21G (d, p) level to derive the optimized geometry and vibrational wave numbers of normal modes of $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ using Gaussian 09W program package [28]. Molecular geometries were fully optimized by Berny’s optimization algorithm using redundant internal coordinates. The optimized structures were confirmed to be minimum energy conformations. Harmonic vibrational wave numbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies (ZPVE). At the optimized structure of the $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$, no imaginary frequencies were obtained, proving that a true minimum on the potential energy surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints.

Results and discussion

Description of structure

An ORTEP view of coordination complex $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ is shown in Fig. 1. The asymmetric unit of $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ complex consists of one cadmium atom, two phenanthroline and two nitrate groups. The $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ complex crystallizes in monoclinic space group $C 2/c$ with four equivalent molecules in the unit cell. Packing arrangement of $[\text{Cd}(\text{phen})_2(\text{NO}_3)_2]$ complex along a -, b - and c -axes is available in supplementary information S1–S3. The cadmium atom is eight coordinated with four nitrogen donors from two bidentate 1,10-phenanthroline ligands and four oxygen atoms of two bidentate nitrate anions. The ligands, 1,

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