CZU: 544.142.3:535.37 **https://doi.org/10.59295/sum1(191)2026_42**

SYNTHESIS, IR AND PL SPECTRA OF NOVEL COMPLEXES $[ZnL^1(CH_3COO)_2]\cdot 2H_2O$ AND $[CdL^1(CH_3COO)_2]\cdot 3H_2O$

Lidia CUBA,
Ion BULHAC,
Moldova State University

Vladislav GHENEA,
Moldova State University,
Technical University of Moldova

Ion CULEAC,
Moldova State University

Transition metal d^{10} complexes $[ZnL^1(CH_3COO)_2]\cdot 2H_2O$ and $[CdL^1(CH_3COO)_2]\cdot 3H_2O$ have been synthesized and characterized by infrared (IR) and photoluminescence (PL) spectroscopy. Under near-UV irradiation the powder samples of two complexes exhibit a strong emission in the spectral range ~ 460-700 nm, with no specific splitting, while the ligand itself shows no luminescence. The coordination of the ligand with Zn(II) or Cd(II) ions within the complexes leads to appearance of strong ligand-centered fluorescence emission in the visible domain. The bright-green luminescence in both complexes is due to the considerable reduction of radiationless rate constants in comparison with the free ligand. The relative intensities of Zn(II) compound is higher than that of Cd(II) compound, similarly as reported in the literature. The relationships between the IR and PL characteristics of Zn(II) and Cd(II) compounds are discussed. Investigated Zn(II) and Cd(II) complexes appear as promising materials for green-emitting components in digital display screens or white-light emitters.

Keywords: *d^{10} metal ions, Zn(II) complex, Cd(II) complex, ligand, photoluminescence, optical transitions, white-light emitters.*

SINTEZA, SPECTRELE IR ŞI PL ALE NOILOR COMPLECŞI [ZnL1(CH3COO)2]·2H2O ŞI [CdL1(CH3COO)2]·3H2O

Compușii coordinativi $[ZnL^1(CH_3COO)_2]\cdot 2H_2O$ și $[CdL^1(CH_3COO)_2]\cdot 3H_2O$ au fost sintetizați și caracterizați prin spectroscopia în infraroșu (IR) și spectroscopia de fotoluminescență (PL). La iradierea cu un fasciul din domeniul UV apropiat, acești compuși prezintă o emisie puternică cu o bandă largă în domeniul ~ 460-700 nm, în timp ce ligandul în sine nu prezintă luminescență. Coordinarea ligandului cu ionii de Zn(II) sau Cd(II) conduce la apariția unei emisii puternice în domeniul vizibil, centrate pe ligand. Luminescența verde-intensă a complecșilor de Zn(II) sau Cd(II) se datorează reducerii considerabile a ratei proceselor neradiative comparativ cu ligandul liber. Intensitatea relativă a emisiei pentru compusul de Zn(II) este superioară față de intensitatea emisiei compusului de Cd(II), similar cu datele din literatură. Este examinată corelația dintre spectrele IR și proprietățile de fotoluminescență ale compușilor de Zn(II) și Cd(II). Complecșii investigați reprezintă materiale promițătoare pentru aplicații în ecranele de afișaj digitale sau **în** sursele de lumină albă.

Cuvinte-cheie: *ioni metalici d^{10}, complex Zn(II), complex Cd(II), ligand, fotoluminescență, tranziții optice, surse de lumină albă.*

Introduction

In recent years considerable research efforts have been devoted to coordination compounds based on transition metals (the group 12 elements) and organic ligands. Of particular interest are coordination compounds containing d^{10} metal ions, such as Zn(II) ($3d^{10}$) and Cd(II) ($4d^{10}$), which have been extensively investigated due to their important roles in biological systems and their attractive photophysical properties [2, 4, 12, 21].

Both Zn(II) and Cd(II) ions possess a closed-shell d^{10} electronic configuration, which results in diamagnetic behaviour and the absence of *d–d* electronic transitions. Consequently, their optical properties are predominantly governed by ligand-centered (LC) or charge-transfer transitions.

Among group 12 metal complexes, Zn(II) compounds have received particular attention because zinc is abundant, relatively inexpensive, and generally regarded as environmentally benign, making Zn(II)-based materials attractive "green" alternatives [3]. Owing to the wide variety of possible coordination numbers, geometries, and molecular architectures, both Zn(II) and Cd(II) coordination compounds exhibit remarkable versatility in their chemical and luminescent properties [3, 6, 17, 20]. In addition, Zn(II) ions play essential roles in numerous biological processes, including the functioning of the nervous and immune systems [21].

Both Zn(II) and Cd(II) ions readily coordinate with a broad range of ligands, including N-, O-, and S-donor ligands, as well as mixed-donor systems. This versatility enables the rational design of diverse supramolecular architectures such as metal–organic frameworks (MOFs), coordination polymers, and luminescent hydrogels [22]. Coordination compounds of Zn(II) and Cd(II) consist of a central divalent metal ion surrounded by ligand molecules or ions, which are bound through coordinate covalent bonds formed by donation of electron pairs from the ligands to the metal center. In particular, Cd(II), similar to Zn(II), possesses a fully filled *d* shell ($4d^{10}$) and shows a strong tendency to form stable coordination compounds.

Cd(II) ions are characterized by a relatively large ionic radius and flexible coordination numbers, typically ranging from four to eight. Depending on the nature of the ligands, Cd(II) complexes may adopt a wide variety of coordination geometries, including tetrahedral, octahedral, trigonal, square-pyramidal, or bicapped trigonal-prismatic arrangements [2]. These structural features enable fine tuning of supramolecular architectures and photophysical properties. In particular, emission colour can be efficiently modulated through ligand design, substitution effects, coordination geometry, solvent interactions, or encapsulation, making Cd(II) complexes promising candidates for multicolour optical sensors and luminescent markers.

Furthermore, as a heavy metal, Cd(II) induces strong spin–orbit coupling (SOC) in ligand-centered excited states, which facilitates intersystem crossing (ISC) and increases the probability of phosphorescence from triplet states. Many Cd(II) coordination compounds, especially those containing carboxylate, thiolate, or aromatic ligands, exhibit high photoluminescence quantum yields. This behaviour is often attributed to efficient ligand-centered or charge-transfer emission and to the suppression of nonradiative deactivation pathways due to rigid coordination environments. Because Zn(II) and Cd(II) complexes frequently display intense blue–green emission, they can, in some cases, serve as alternatives to lanthanide(III) compounds, which typically exhibit weak luminescence in this spectral region.

Zn(II) and Cd(II) complexes are therefore often investigated in parallel, as they provide a well-defined comparative platform for assessing the influence of metal ion size, coordination geometry, and structural rigidity on the properties of coordination compounds, particularly in luminescent materials and molecular sensing applications [18]. In this context, the present work focuses on the synthesis and comparative infrared (IR) and photoluminescence (PL) characterization of Zn(II) and Cd(II) coordination compounds, aiming at a deeper understanding of their photoluminescence behaviour with respect to potential practical applications.

1. Materials and methods

1.1. Materials

All the reagents used in this study were obtained from commercial sources and employed as received without additional purification. As starting materials isonicotinic hydrazide, *o*-phthalaldehyde, methanol, diethyl ether, $Zn(CH_3COO)_2 \cdot 2H_2O$, $Cd(CH_3COO)_2 \cdot 2H_2O$ were used.

1.2. Synthesis of L[1]

Isonicotinic hydrazide (0.112 g, 8 mmol) was dissolved in a methanol (5 mL) with permanent stirring and heating. Then a hot solution of *o*-phthalic dicarboxaldehyde (0.052 g, 4 mmol) in a methanol (5 mL) was added. The resulting mixture was stirred and heating for about 1h. The white precipitate was filtered off, washed with methanol, diethyl ether and then dried in air. Yield: 0.090 g, 60%. Elemental analysis was calculated for $C_{20}H_{16}N_6O_2$ (372.380 g/mol): C 64.51, H 4.33, N 22.57; found C 65.48, H 4.17, N 22.77%.

IR (ν, cm^{-1}) 3229 m, 3154 sh, 3069 m, 3047 m, 2949 sh, 2842 w, 2611 w, 2198 w, 1950 w, 1659 vs, 1598 m, 1584 m, 1550 vs, 1480 m, 1444 w, 1408 m, 1369 m, 1331 w, 1286 vs, 1217 m, 1157 w, 1141 m, 1112 w, 1063 sh, 1055 s, 993 w, 960 w, 943 m, 919 m, 862 w, 844 m, 828 sh, 754 s, 747 m, 705 w, 685 sh, 671 sh, 623 w, 542 vw, 516 vw, 492 w, 465 vw.

1.3. Synthesis of $[ZnL^1(CH_3COO)_2]\cdot 2H_2O$

Isoniazid (0.028 g, 2 mmol) was dissolved in a methanol (5 mL) with permanent stirring and heating. Then a hot solution of *o*-phthalic dicarboxaldehyde (0.013 g, 1 mmol) in a methanol (5 mL) was added. After 5 min was added hot solution of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.022 g, 1 mmol) in a methanol (5 mL). The resulting solution was stirred and heating for about 1h. After cooling, a yellow precipitate was separated upon filtration, washed with methanol, diethyl ether and dried in air. Yield: 0.049 g, 84%. Elemental analysis was calculated for $C_{24}H_{26}N_6O_8Zn$ (591.889 g/mol): C, 48.70; H, 4.43; N, 14.19; Zn, 11,05; found: C, 49.27; H, 3.34; N, 15.73; Zn, 11,50 %. IR (ν, cm^{-1}): 3352 br, 3192 br, 3079 br, 2958 m, 2503 w, 1662 w, 1617 m, 1598 vs, 1574 s, 1516 vs, 1484 vs, 1418 m, 1367 vs, 1315 m, 1271 w, 1238 m, 1153 m, 1085 w, 1057 m, 1031 s, 1022 s, 963 m, 948 m, 935 m, 894 m, 847 m, 804 w, 761 s, 750 s, 699 vs, 666 vw, 581 w, 557 w, 520 w, 469 vw, 445 w, 421 vw.

1.4. Synthesis of $[CdL^1(CH_3COO)_2]\cdot 3H_2O$

Isoniazid (0.168 g. 12 mmol) was dissolved in a methanol (5 mL) with permanent stirring and heating. Then a hot solution of *o*-phthalic dicarboxaldehyde (0.088 g, 6 mmol) in a methanol (5 mL) was added. After 5 min was added hot solution of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.069 g, 3 mmol) in a methanol (5 mL). The resulting solution was stirred and heating for about 1h. After cooling, a yellow precipitate was separated by filtration, washed with methanol, diethyl ether and air dried. Yield: 0.110 g, 56%. Elemental analysis was calculated for $C_{24}H_{28}N_6O_9Cd$ (656.925 g/mol): C, 43.88; H, 4.29; N, 12.79; Cd, 17.11; found C, 43.79; H, 4.35; N, 13.12; Cd, 17.05%. IR (ν, cm^{-1}): 3600-3350 br, 3329 m, 3247 m, 3052 w, 2976 w, 2937 w, 2898 w, 1659 s, 1610 m, 1539 vs, 1498 m, 1464 sh, 1453 m, 1411 vs, 1373 m, 1335 m, 1311 m, 1261 m, 1224 s, 1181 s, 1159 vw, 1144 m, 1111 m, 1065 m, 1049 w, 1017 s, 945 m, 910 m, 896 m, 851 m, 830 s, 767 s, 739 m, 707 vw, 695 m, 675 m, 647 m, 636 m, 619 m, 541 w, 529 w, 465 w.

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a GmbH Vario-EL-III-CHNOS elemental analyser at the Centre for physical and inorganic chemistry of the Institute of Chemistry.

Photoluminescence characteristics were investigated at room temperature. The low-resolution excitation spectra (0.125 nm) were registered with an MDR-23 single grating monochromator (LOMO, St. Petersburg, Russia) as an excitation source and a double grating spectrometer DFS-52 (LOMO, St. Petersburg, Russia) for collecting the PL emission. A halogen lamp OSRAM 64623 HLX 12V 100W was used as a light excitation source. The spectra were corrected for the instrument spectral sensitivity. Low resolution emission spectra (0.125 nm) were registered with an MDR-23 single grating monochromator and a Hamamatsu photomultiplier head H9319-02-12 (Hamamatsu Photonics K.K., Japan) in a photon counting mode. PL emission spectra were registered with a Thorlabs collimated laser diode module (CPS405 405 nm, 4.5 mW) as an excitation source.

IR spectra were registered with a Perkin-Elmer 100 FT-IR spectrometer at room temperature using ATR technique (4000-650 cm^{-1}) and in Nujol (650-400 cm^{-1}). Intensities are presented as: br = broaded, sh = shoulder, vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

2. Results and Discussion

2.1. Infrared spectra

The IR spectrum of the ligand (L^1) (Figure 1) contains an absorption band at 3229 cm^{-1} of medium intensity, assigned to ν(N-H) vibrations; ν(C-H) absorption bands at 3069 cm^{-1} (ν_{as}) and 3047 cm^{-1} (ν_s). The absorption band at 1659 cm^{-1}, attributed to ν(C=O) vibrations, has the highest intensity in the spectrum. A high-intensity band at 1550 cm^{-1} is assigned to δ(NH)+ν(C-N) vibrations, also known as the “amide II band”, while the intense band at 1286 cm^{-1} corresponds to N-C=O vibrations [14].

The medium intensity absorption bands at 1584, 1480 and 747 cm^{-1} indicate the 1,2-substitution type in the benzene ring [15]. The deformation vibrations C-H in-plane $\delta_{pl.}$(CH) in the aromatic rings with 1,2/1,4

substitution type occurred at 1217, 1055 and 993 cm^{-1}. The absorption bands at 844 cm^{-1} and 754 cm^{-1} are attributed to the C-H out-of-plane δ(CH) vibrations of two adjacent hydrogen atoms in the pyridine ring (1,4 substitution type) and of four adjacent hydrogen atoms in the benzene ring (1,2 substitution type), respectively.

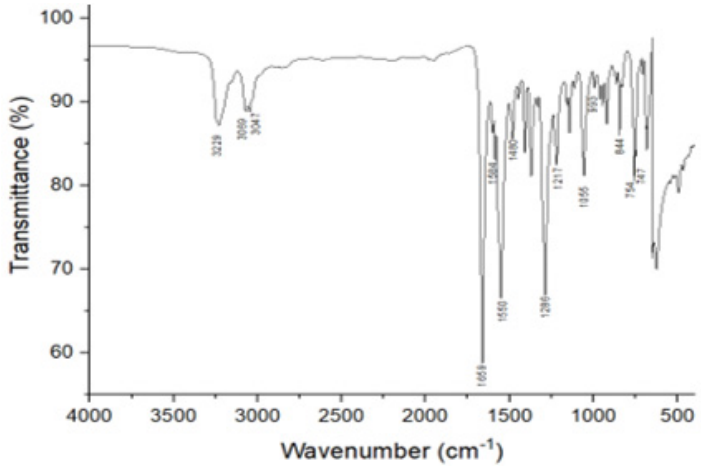

Figure 1. Infrared spectrum of the ligand L1

The IR spectrum of Cd(II) complex (Figure 2) contains a relatively narrow medium-intensity band at 3329 cm^{-1}, attributed to associated ν(OH) vibrations, and a very narrow band of higher intensity at 3247 cm^{-1}, attributed to the ν(NH) vibrations. A high intensity band at 1659 cm^{-1} is also observed, which is attributed to the ν(C=O) vibrations, matching the position of this band in the IR spectrum of L^1. The carboxylate ions CH_3COO^- in this spectrum absorb at 1539 and 1411 cm^{-1}, showed a highest intensity and broadest than the other bands. Considering that the first value representing the ν_{as} vibrations, and the second - ν_s(C---O) vibrations in carboxylate ions $\Delta(\nu_{as}-\nu_s)$=1539 – 1411= 128 cm^1), we can conclude the bidentate mode of coordination to the Cd(II) ion. Medium-intensity bands at 1610, 1498 and 1453 cm^{-1} correspond to stretching vibrations (C=C). The weaker absorption bands at 1464 and 1373 cm^{-1} are assigned to $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ vibrations, respectively. The absorption bands at 1261 and 1065 cm^{-1} are caused by the 1,2/1,4 substitution type in the aromatic rings [15]. The absorption bands of deformation oscillations C-H in-plane δ_{pl}(CH) in aromatic rings with 1,2/1,4 substitution can be observed at 1261, 1224, 1065 and 1017 cm^{-1}; but out-of-plane for two adjacent hydrogen atoms (1,4 substitution type) – at 830 cm^{-1}, and for four adjacent hydrogen atoms (1,2 substitution type) – at 767 cm^{-1}.

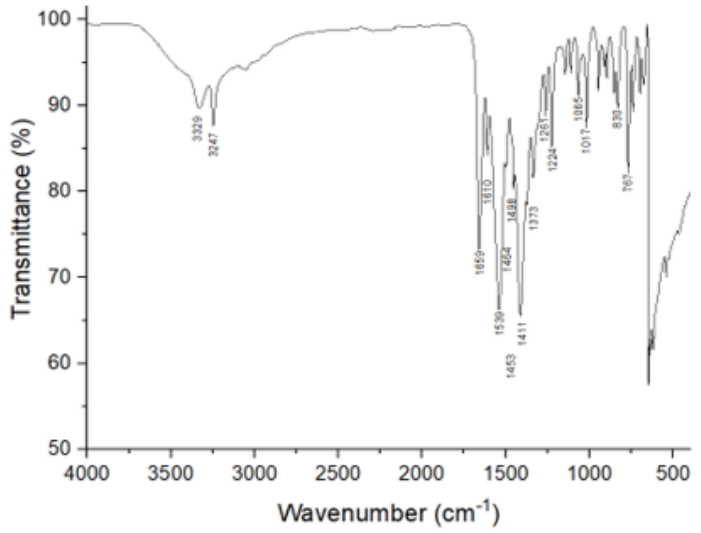

Figure 2. Infrared spectrum of the complex [CdL1(CH3COO)2]·3H2O

The IR spectrum of Zn(II) compound (Figure 3) differs significantly from that of the Cd(II) compound. The ν(OH) at 3352 cm^{-1} and ν(NH) at 3192 cm^{-1} absorption bands are substantially broader compared to those in the spectrum of the Cd(II) compound, which leads to the conclusion that in the Zn(II) complex these vibrations are associated more strongly. The absorption band ν(C=O), present in both the spectra of L^1 and Cd(II) compound spectra at 1659 cm^{-1}, is absented here, but a new absorption band of the highest intensity appears at 1370 cm^{-1}. So the band ν(C=O) is transformed to ν(C---O) caused by the electronic density delocalization effect as a result of the formation of metallocycles, and shifts to the low-frequency region in this spectrum. The absorption bands at 1617 and 1316 cm^{-1} are assumed to represent the ν_{as} and ν_s vibrations of the monodentately coordinated carboxylate ions. The high-intensity absorption band at 1520 cm^{-1} is attributed to δ(NH)+ν(C-N) vibrations (amide II band). Notably, the most intense and very broad bands at 1539 and 1411 cm^{-1}, which are present in the spectrum of the Cd(II) complex, are absent in the spectrum of the Zn(II) complex. The deformation vibrations C-H in-plane of the aromatic rings $\delta_{pl.}$(C-H) appear as bands at 1240, 1058 and 962 cm^{-1}; and the non-planar for two adjacent hydrogen atoms – 848 cm^{-1}, and for four adjacent hydrogen atoms – 701

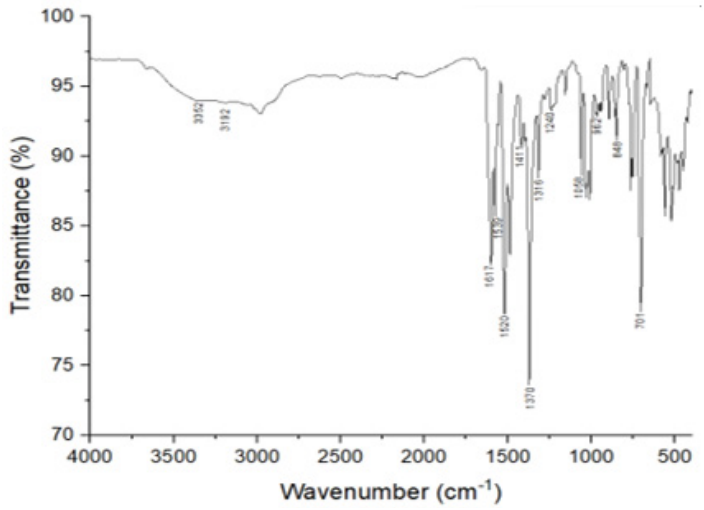

Figure 3. Infrared spectrum of the complex [ZnL1(CH3COO)2]·2H2O

cm^{-1}. Based on the IR spectral data, it can be assumed that in the case of the Zn(II) complex, the carboxylate ion COO^- most likely coordinates in the monodentate manner $\Delta(\nu_{as}-\nu_s)$ = 1617 – 1316 = 301 cm^{-1}) with the highest value of $\Delta(\nu_{as}-\nu_s)$ among all coordination types and the ionic form of COO^- [15].

2.2. Photoluminescence properties of the complexes

The photoluminescence (PL) properties of the Zn(II) and Cd(II) coordination compounds were investigated on powder samples at room temperature under excitation of laser beam 405 nm. The excitation spectrum of the Zn(II) complex, recorded by monitoring the emission at 506 nm is represented in Figure 4. A broad excitation band extending from approximately 330 to 500 nm is observed, with a pronounced maximum at around 469 nm and a weak shoulder near 398 nm. Such a broad excitation profile is characteristic of ligand-centered or charge-transfer transitions. The weak shoulder at ca. 398 nm can be tentatively assigned to a higher-energy ligand-centered π→π* transition.

Given the d^{10} electronic configuration of the Zn(II) ion, *d–d* transitions are absent and the metal center does not contribute directly to the electronic absorption. Consequently, the observed luminescence originates from the organic ligand framework or from ligand-based charge-transfer states, such as ligand-centered (LC) or, less frequently, ligand-to-ligand charge-transfer (LLCT) states, as reported for similar Zn(II) systems [8,9,16]. The proximity of the excitation maximum (~ 469 nm) to the onset of the emission band (~ 506 nm) indicates a relatively small Stokes shift, consistent with fluorescence arising from a ligand-centered excited singlet state (π*→π).

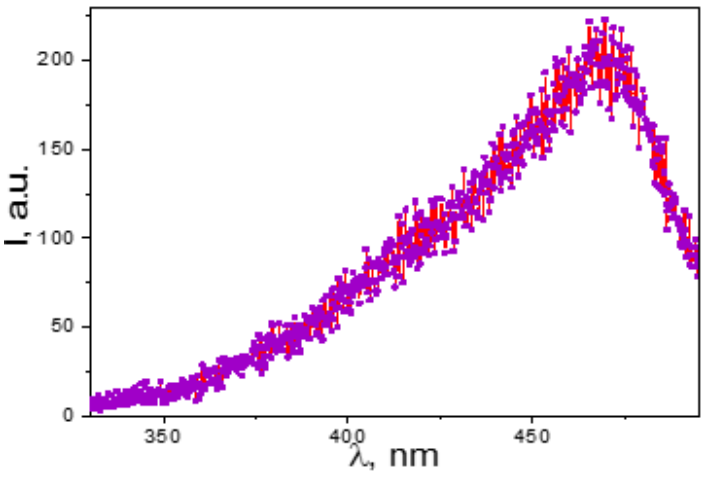

Figure. 4. Excitation spectrum of Zn(II) complex powder sample recorded for the emission band at 506 nm

Upon excitation at 405 nm, both Zn(II) and Cd(II) complexes exhibit intense visible luminescence, readily observable by the naked eye. The PL emission spectra of the complexes are presented in Figure 5. Under near-UV excitation, both compounds emit broadly in the green–red spectral region, whereas the free ligand L^1 shows no detectable emission under identical conditions. This behavior clearly indicates that coordination to Zn(II) or Cd(II) ions is essential for activating the luminescence.

The emission spectrum of the Zn(II) complex consists of a broad, asymmetric band spanning approximately 460–720 nm, with a dominant maximum at ~507 nm and a shoulder at around 546 nm. A steep rise in emission intensity is observed between 450 and 507 nm, followed by a gradual decay toward longer wavelengths. In contrast, the Cd(II) complex displays a significantly lower emission intensity—more than two times weaker than that of the Zn(II) analogue—and exhibits a broad, nearly featureless emission band in the same spectral range, with a flat maximum centered near 530 nm and weak shoulders at approximately 485 and 608 nm.

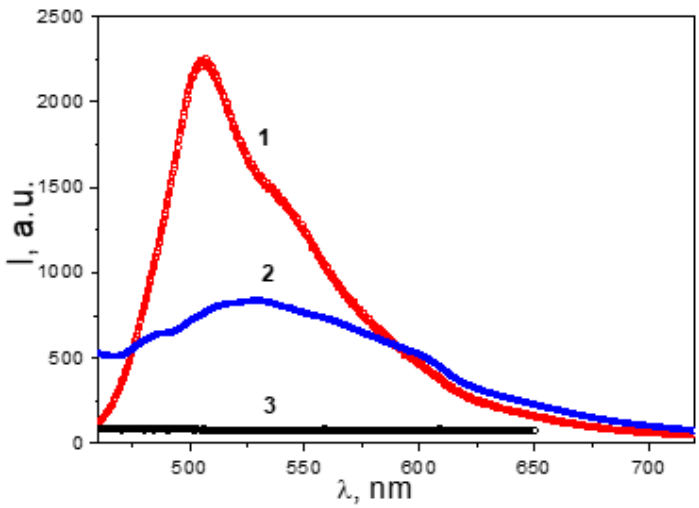

Figure 5. PL emission spectra of coordination compounds registered under excitation of 405 nm laser beam: 1 - [ZnL1(CH3COO)2]·2H2O; 2 - [CdL1 (CH3COO)2]·3H2O; 3 - L1

Since the free ligand is non-emissive under 405 nm excitation, while both metal complexes exhibit pronounced luminescence, the emission can be attributed to coordination-induced effects. Zn(II) and Cd(II) ions possess closed-shell d^{10} configurations and are therefore not intrinsically emissive. However, metal coordination significantly rigidifies the ligand framework, suppressing nonradiative decay pathways associated with ligand vibrations and rotations [1]. As a result, ligand-centered fluorescence is enhanced upon complexation. In addition, coordination may facilitate intraligand charge-transfer (ILCT) or LLCT processes, contributing to the observed emission [13].

The presence of a single, broad emission band for both Zn(II) and Cd(II) complexes suggests that the luminescence originates from π→π* transitions within an extended conjugated ligand system or from intramolecular charge-transfer (ICT) states [8]. The broad emission tail extending into the red region points to inhomogeneous broadening, which may arise from structural disorder, multiple emissive conformations, or intermolecular interactions in the solid state.

For the Zn(II) complex, the intense maximum at ~ 507 nm is attributed to radiative decay from the lowest singlet excited state ($S_1 \rightarrow S_0$). The shoulder at ~ 546 nm may originate from vibronic coupling or from the presence of additional emissive species, such as different conformers or aggregated states.

It is well established that Zn(II) chelate complexes often exhibit significantly enhanced fluorescence compared to their free ligands [11]. In the uncoordinated state, organic ligands typically possess flexible structures and multiple vibrational degrees of freedom, which favour nonradiative relaxation and result in low quantum yields. Coordination to Zn^{2+} or Cd^{2+} ions increases structural rigidity and reduces these nonradiative pathways. As neither Zn^{2+} nor Cd^{2+} ions support *d–d* transitions, the emission remains ligand-centered and can be assigned to π*→π, π*→n, ILCT, or LLCT transitions. Such delocalized electronic transitions naturally give rise to broad, structureless emission bands, as observed in Figure 5.

The luminescence mechanism in Zn(II) and Cd(II) complexes differs fundamentally from that of lanthanide-based systems, such as Eu(III) complexes. In lanthanide compounds, emission arises from intra-4f radiative transitions, producing sharp, line-like spectra with characteristic Stark splitting [5]. In contrast, Zn(II) and Cd(II) complexes are often described as spectroscopically silent with respect to metal-centered transitions, due to their closed-shell electronic configurations, [Ar]$3d^{10}$ for Zn^{2+}, and [Kr]$4d^{10}$ for Cd^{2+}. As a result, the metal ions primarily act as structural scaffolds that modulate ligand geometry and electronic structure rather than serving as emissive centers.

In both Zn(II)/Cd(II) and lanthanide complexes, photoexcitation initially occurs within the ligand. However, in Zn(II) and Cd(II) systems, the excited ligand has no energetically accessible metal-centered states to which energy can be transferred. Because Zn^{2+} ($3d^{10}$) and Cd^{2+} ($4d^{10}$) have no low-lying metal-centered excited states, the PL spectrum reflects ligand-based or charge-transfer processes, not d–d transitions [10]. Consequently, the excited state relaxes radiatively via ligand-based fluorescence or, in some cases, phosphorescence, leading to broad molecular emission bands. The photoluminescent properties of these complexes are therefore governed by ligand electronic structure, coordination-induced rigidity, and steric effects [7,19]. Unlike rare-earth ions, Zn(II) and Cd(II) complexes lack atomic-like transitions and do not exhibit Stark splitting, as their emission originates from delocalized molecular orbitals rather than localized atomic states.

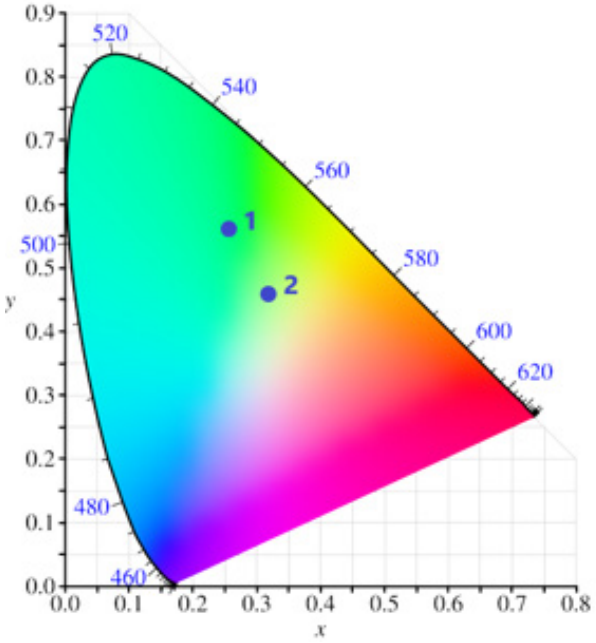

Figure 6. CIE colour coordinate plot showing the x,y coordinates of the emission in Zn(II) and Cd(II) complexes. The emission colour is marked by the blue circles. *(1)* Zn(II) complex (x = 0.2785; y = 0.5604); *(2)* Cd(II) complex (x = 0.3286; y = 0.4555)

The broad emission bands observed for both complexes can be further attributed to strong coupling between the electronic excited states and molecular vibrations of the organic ligand. Such electron–phonon interactions lead to vibrational and inhomogeneous broadening, effectively washing out fine spectral features. Additional broadening may arise from environmental effects, including local polarity variations, molecular disorder, and intermolecular interactions in the solid state. Particularly, comparing the Zn(II) vs Cd(II) complex, Cd(II) shows broader, red-shifted emission probably due to heavier atom and larger coordination sphere. Additionally, higher PL intensity for the Zn(II) complex may indicate on more rigid framework, while narrower bands for this complex suggest reduced vibrational coupling [9].

The calculated CIE (Commission Internationale de l'Éclairage) chromaticity coordinates, derived from the PL spectra (Figure 5), are shown in Figure 6. The Zn(II) complex exhibits coordinates of x = 0.2785 and y = 0.5604, while the Cd(II) complex shows x = 0.3286 and y = 0.4555. Both values fall within the yellow–green region of the chromaticity diagram, indicating that these materials may be suitable as green-emitting components for applications in RGB-based devices or white-light-emitting systems when combined with complementary blue and red emitters.

Conclusions

The d^{10} transition-metal coordination compounds $[ZnL^1(CH_3COO)_2]\cdot 2H_2O$ and $[CdL^1(CH_3COO)_2]\cdot 3H_2O$ were successfully synthesized and characterized by infrared and photoluminescence spectroscopy. Under near-UV excitation, the powder samples of both complexes exhibit intense visible emission, characterized by broad, structureless bands extending over the 460–700 nm spectral range.

In contrast, the free ligand L^1 shows no detectable luminescence under identical excitation conditions. The emergence of strong emission upon coordination to Zn(II) and Cd(II) ions clearly demonstrates that metal–ligand complexation plays a key role in activating and enhancing the photoluminescent response. **The observed bright green emission** originates from ligand-centered excited states and is attributed primarily to coordination-induced rigidification of the ligand framework, which effectively suppresses nonradiative deactivation pathways relative to the free ligand.

A comparative analysis reveals that the Zn(II) complex exhibits higher emission intensity than its Cd(II) analogue, in agreement **with trends reported in the literature for related d^{10} metal systems**. Differences in photoluminescence efficiency are likely related to variations in coordination geometry, ligand–metal interactions, and excited-state relaxation dynamics. The relationships between the PL characteristics of the Zn(II) and Cd(II) complexes have been discussed in detail. Owing to their broad fluorescence bands spanning the green region of the visible spectrum, the investigated Zn(II) and Cd(II) complexes appear to be promising candidates for use as green-emitting components in RGB-based devices or as emissive materials in white-light-emitting systems.

Bibliography:

1. Aragoni, M., Arca, M., Bencini, A., Caltagirone, C., Garau, A., Isaia, F., Light, M., Lppolis, V., Lodeiro, C., Mameli, M., Montis, R., Mostallino, M., Pintus, A., Puccioni, S. *Zn2+/Cd2+ optical discrimination by fluorescent chemosensors based on 8-hydroxyquinoline derivatives and sulfur-containing macrocyclic units.* Dalton Transactions, 2013, 42, pp. 14516–14530. DOI: https://doi.org/10.1039/c3dt51292d

2. Barbieri, A., Accorsi, G., Armaroli, N. *Luminescent complexes beyond the platinum group: the d10 avenue.* Chemical Communications, 2008, pp. 2185–2193. DOI: https://doi.org/10.1039/b716650h
3. Bolla, G., Chen, Q., Gallo, G., Park, I.-H., Kwon, K., Wu, X., Xu, Q.-H., Loh, K., Chen, S., Dinnebier, R., Ju, W., Vittal, J. *Multifunctional properties of a zinc(II) coordination complex.* Crystal Growth and Design, 2021, 21, pp. 3401–3408. DOI: https://doi.org/10.1021/acs.cgd.1c00179
4. Chukwuma, C., Mashele, S., Eze, K., Matowane, G., Islam, S., Bonnet, S., Noreljaleel, A., Ramorobi, L. A comprehensive review on zinc(II) complexes as anti-diabetic agents: the advances, scientific gaps and prospects. *Pharmacological Research,* 2020, 155, 104744. DOI: https://doi.org/10.1016/j.phrs.2020.104744
5. Culeac, I., Verlan, V., Bordian, O., Melnic, E., Podgornii, D., Bulhac, I., Cojocaru, I., Moise, C., Ghenea, V., Siminel, A., Enachescu, M. Structure and photoluminescence properties of coordination compound [Eu2(o-MBA)6(phen)2] with high quantum yield. *Journal of Luminescece,* 2024, 276, 1208554. DOI: https://doi.org/10.1016/j.jlumin.2024.120854
6. Diana, R., Panunzi, B. The role of zinc(II) ion in fluorescence tuning of tridentate pincers: a review. *Molecules,* 2020, 25, 4984. DOI: https://doi.org/10.3390/molecules25214984
7. Gennari, M., Lanfranchi, M., Marchio, L. Novel carbon-centered heteroscorpionate ligands: Cu(I) complexes and luminescence properties. *Inorganica Chimica Acta*, 2009, 362, pp. 4430–4438. DOI: https://doi.org/10.1016/j.ica.2009.05.014
8. Kokina, T., Shekhovtsov, N., Vasilyev, E., Glinskaya, L., Mikheylis, A., Plyusnin, V., Tkachev, A., Bushuev, M. *Efficient emission of Zn(II) and Cd(II) complexes with nopinane-annelated 4,5-diazafluorene and 4,5-diazafluoren-9-one ligands: how slight structural modification alters fluorescence mechanism.* Dalton Transactions, 2023, 52, pp. 7429–7446. DOI: https://doi.org/10.1039/D3DT00904A
9. Korolenko, S., Zhuravlev, K., Tsaryuk, V., Kubasov, A., Avdeeva, V., Malinina, E., Burlov, A., Divaeva, L., Zhizhin, K., Kuznetsov, N. Crystal structures, luminescence, and DFT study of mixed-ligand Zn(II) and Cd(II) complexes with phenyl-containing benzimidazole derivatives with linker C=N or N=N group. J*ournal of Luminescence,* 2021, 237, pp. 118156–118168. DOI: https://doi.org/10.1016/j.jlumin.2021.118156
10. Kubler, J., Pfund, B., Wenger, O. Zinc(II) complexes with triplet charge-transfer excited states enabling energy-transfer catalysis, photoinduced electron transfer, and upconversion. *Journal American Chemical Society Au,* 2022, 2, pp. 2367–2380. DOI: https://doi.org/10.1021/jacsau.2c00442
11. Larionov, S., Kokina, T., Plyusnin, V., Glinskaya, L., Tkachev, A., Bryleva, Y., Kuratieva, N., Rakhmanova, M., Vasilyev, E. Synthesis, structure and photoluminescence of Zn(II) and Cd(II) complexes with pyridophenazine derivative. *Polyhedron,* 2014, 77, pp. 75–80. DOI: http://dx.doi.org/10.1016/j.poly.2014.04.011
12. Lee, L., Lo, K. Shining new light on biological systems: luminescent transition metal complexes for bioimaging and biosensing applications. *Chemical Reviews*, 2024, 124, pp. 8825–9014. DOI: https://doi.org/10.1021/acs.chemrev.3c00629
13. Majumder, A., Rosair, G., Mallick, A., Chattopadhyay, N., Mitra, S. Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N,N,O-tridentate Schiff base N-2-pyridylmethylidene-2-hydroxy-phenylamine. *Polyhedron*, 2006, 25, pp. 1753–1762. DOI: https://doi.org/10.1016/poly.2005.029
14. Nacanisi, K. *IR spectre and structure of organic compounds.* M., 216 p. (in Russian).
15. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2009, 416 p. ISBN: 978-0-471-74493-1.
16. Narea, P., Cisterna, J., Cardenas, A., Amo-Ochoa, P., Zamora, F., Climent, C., Alemany, P., Conejeros, S., Llanos, J., Brito, I. Crystallization Induced Enhanced Emission in Two New Zn(II) and Cd(II) Supramolecular Coordination Complexes with the 1-(3,4-Dimethylphenyl)-5-Methyl-1H-1,2,3-Triazole-4-Carboxylate Ligand. *Polymers,* 2020, 12, 1756. DOI: https://doi.org/10.3390/polym12081756
17. Omar Ali, A.-A., Ahmed, R., Al-Karawi, A., Marah, S., Kansiz, S., Sert, Y., Jaafar, M., Dege, N., Poyraz, E., Ahmed, A., Ozen, T., Loukil, M., Jwad, R. Designing of two new cadmium(II) complexes as bioactive materials: synthesis, X-ray crystal structures, spectroscopic, DFT, and molecular docking studies. *Journal of Molecular Structures,* 2023, 1290, 135974. DOI: https://doi.org/10.1016/j.molstruc.2023.135974

18. Parmar, B., Bisht, K., Rachuri, Y., Suresh, E. Zn(II)/Cd(II) based mixed ligand coordination polymers as fluorosensors for aqueous phase detection of hazardous pollutants. *Inorganic Chemistry Frontiers*, 2020, 7, pp. 1082–1107. DOI: https://doi.org/10.1039/c9qi01549c
19. Rashamuse, T., Mohlala, R., Coyanis, E., Magwa, N. A review: blue fluorescent zinc (II) complexes for OLEDs – a last five-year recap. *Molecules*, 2023, 28(13), pp. 5272–5288. DOI: https://doi.org/10.3390/molecules28135272
20. Scaeteanu, G., Maxim, C., Badea, M., Olar, R. Zinc(II) carboxylate coordination polymers with versatile applications. *Molecules*, 2023, 28(3), 1132. DOI: https://doi.org/10.3390/molecules28031132
21. Tian, X., Hussain, S., Pace, C., Ruiz-Perez, L., Battglia, G. ZnII complexes for bioimaging and correlated applications. *Chemistry an Asian Journal,* 2019, 14, pp. 509–526. DOI: https://doi.org/10.1002/asia.201801437
22. Zhang, J., Gong, L., Feng, J., Wu, J., Zhang, C. Two luminescent Zn(II)/Cd(II) metal-organic frameworks as rare multifunctional sensors. *New Journal of Chemistry*, 2017, 41, pp. 8107–8117. DOI: https://doi.org/10.1039/c7

N. B.: *We acknowledge financial support by the Ministry of Education and Research of the Republic of Moldova through research subprograms 010602 “Synthesis and study of new materials based on coordination compounds with polyfunctional ligands with useful properties in medicine, biology and technology”, and 011201 “Functional 2D and 3D oxychalcogenide materials, metals and polymers with advanced magnetic, photoelectric, optical and bioactive properties for applications in spintronics, optoelectronics and biomedicine”.*

Data about the authors:
Ion BULHAC, dr. habilitate, assoc. prof., head of laboratory, Institute of Chemistry, Moldova State University.
ORCID: 0000-0002-2437-2875
E-mail: ionbulhac@yahoo.com

Lidia CUBA, scientific researcher, Institute of Chemistry, Moldova State University.
ORCID: 0009-0003-3540-2712
E-mail: l-koba@list.ru

Vladislav GHENEA, scientific researcher, Institute of Applied Physics, Moldova State University, PhD student at Technical University of Moldova.
ORCID: 0009-0009-0850-2244
E-mail: vladislav.ghenea@ifa.usm.md

Ion CULEAC, dr., assoc. prof., leading scientific researcher, Institute of Applied Physics, Moldova State University.
ORCID: 0009-0005-3915-2583
E-mail: ionculeac@gmail.com

Presented: 06.02.2026
Reviewed: 19.03.2026
Accepted for publication: 20.05.2026