

SYNTHESIS AND CRYSTAL STRUCTURES OF LUMINESCENT MONONUCLEAR Ni(II) AND Cd(II) COMPLEXES WITH 1,10-PHENANTHROLINE

Ecaterina Tocana^a, Anatolii Siminel^b, Lilia Croitor^{b*}

^aTiraspol State University, 5, Iablocikin str., Chisinau MD2069, Republic of Moldova

^bInstitute of Applied Physics Academy of Sciences of Moldova, 5, Academy str., Chisinau MD2028, Republic of Moldova

*e-mail: croitor.lilia@gmail.com; phone:(+373 22) 738 154; fax:(+373 22) 725 887

Abstract. Two new mononuclear coordination complexes constructed by non-covalent interactions, [Ni(phen)₂(H₂O)₂](ClO₄)₂ (**1**) and [Cd(ClO₄)₂(phen)₂] (**2**), where phen=1,10-phenanthroline, were synthesized and characterized by single-crystal X-ray diffractometry. The structural determination revealed that the coordination geometry around the Ni/Cd centres is distorted octahedral for each complex. In the complexes **1** and **2** the metal atoms have N₄O₂ coordination cores. In **1** the intermolecular OH...O hydrogen bonds, which involve the coordinating water molecules as donors and the perchlorate O atoms as acceptors form zigzag-like hydrogen-bonding chains, which are further assembled *via* π - π stacking interactions between adjacent phen rings, thus forming a supramolecular network structure. In the crystal structure of **2**, π - π stacking interactions are noted between neighbouring hydrophobic phen ligands, yielding 1D supramolecular chains. The luminescence studies show that compound **1** displays blue luminescence, while compound **2** – white-light emission upon excitation with ultraviolet light.

Keywords: supramolecular system, 1,10-phenanthroline, π - π stacking interaction, X-ray, luminescence.

Received: 15 September 2017/ Revised final: 18 October 2017/ Accepted: 20 October 2017

Introduction

Supramolecular aggregates based on small molecules are held together in the crystal by weak attractive non-covalent interactions, such as hydrogen bonding, ionic interactions, metal coordination, π - π stacking or hydrophobic interactions. Non-covalent interactions play an important role in chemistry, physics and especially in biodisciplines [1-3]. They determine the structure of biomacromolecules such as DNA and proteins and are responsible for the molecular recognition process [4,5].

1,10-Phenanthroline (phen) is a bidentate ligand that entails several appealing structural and chemical properties such as rigidity, planarity, aromaticity, basicity, chelating capability that makes it a versatile starting material for supramolecular chemistry. The rigid aromatic phenyl and pyridine rings on phen have the potential to generate π - π and C-H- π stacking interactions, which have great significance in the crystal packing and influence the architecture of the resulting crystal structures. Recently we have reported the synthesis and crystal structure of Cr(III) supramolecular systems containing

phenanthroline and acetylacetonate ligands constructed by combining two or three organizing forces (metal coordination, hydrogen bonds and π - π stacking interactions), which demonstrate metal-to-ligand charge transfer (MLCT) nature. The phen ligand is coordinated to Cr(III) ions to form additional five-member rings, which increase the π - π^* conjugation length and the conformational coplanarity [6].

In this article, we report two mononuclear coordination complexes of phen, [Ni(phen)₂(H₂O)₂](ClO₄)₂ (**1**) and [Cd(ClO₄)₂(phen)₂] (**2**). Their syntheses, crystal structures, and luminescence properties were investigated and discussed.

Experimental

All reagents and solvents were obtained from commercial sources and were used without further purification. *Caution!* Perchlorate salts are dangerous and should be handled with care and only in small quantities. Cadmium salts are carcinogenic and toxic [7]. Emission spectra were recorded for single crystals at room temperature on an Excitation YAG:Nd³⁺ laser, third harmonic

generation, $\lambda = 337$ nm, duration 10 ns, time repetition 10 Hz.

Synthesis of $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (1)

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.30 mg, 0.15 mmol) and 1,10-phenanthroline (18.02 mg, 0.1 mmol) were dissolved in 6 mL of methanol. Then 4 drops of acetylacetone were added. The reaction mixture was stirred for ~ 5 min, filtered off and then slowly cooled to room temperature giving a mixture of blue-violet and pink crystals. The two types of crystals were separated mechanically. Yield of blue-violet crystals: ~55%.

Synthesis of $[\text{Cd}(\text{phen})_2(\text{ClO}_4)_2]$ (2)

$\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (31.00 mg, 0.1 mmol) and 1,10-phenanthroline (18.02 mg, 0.1 mmol) were dissolved in 6 mL of methanol. Then 4 drops of acetylacetone were added. The reaction mixture was stirred for ~5 min, filtered off and then slowly cooled to room temperature giving colourless crystals. Yield: ~33 %.

X-ray structure determination

Diffraction measurements for **1** and **2** were carried out at room temperature on an Xcalibur "Oxford Diffraction" diffractometer equipped with CCD area detector and a graphite monochromator utilizing $\text{MoK}\alpha$ radiation. Final unit cell dimensions were obtained and refined on an entire data set. All calculations to solve the structures and to refine the proposed models were carried out with the SHELXS97 and SHELXL2014 programs [8,9]. For compound **1**

the perchlorate anions are disordered over two positions (80/20% and 65/35% occupancy). Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined by using a riding model.

The figures were produced using the Mercury program [10]. Crystallographic data for new structures reported herein were deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1563783-1563784. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Crystal structure analysis

Both coordination compounds were obtained in the identical synthetic conditions by mixing the warm methanolic solutions of the corresponding starting perchlorate salts, 1,10-phenanthroline and acetylacetonate. The final acetylacetonate-free crystalline solids were precipitated from the slowly cooled solutions. Compound **1** is a blue-violet crystalline solid; in addition to **1** in the same reaction, pink crystals of the known compound $[\text{Ni}(\text{phen})_3](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ [11] were precipitated. The X-ray data and the details of the refinement for both compounds are summarized in Table 1.

Table 1

Crystallographic data and structure refinement details for compounds **1** and **2**.

Parameters	1	2
Compound	1	2
Empirical formula	$\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_4\text{NiO}_{10}$	$\text{C}_{24}\text{H}_{16}\text{CdCl}_2\text{N}_4\text{O}_8$
Formula weight	654.05	671.71
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P-1$
Z	4	1
a (Å)	17.6783(10)	8.2130(9)
b (Å)	8.8563(4)	8.9194(10)
c (Å)	17.5013(12)	9.4431(10)
α (deg)	90	108.185(10)
β (deg)	107.144(7)	105.305(9)
γ (deg)	90	104.568(10)
V (Å ³)	2618.3(3)	1.889
D_c (g/cm ⁻³)	1.659	1.213
μ (mm ⁻¹)	1.011	334
$F(000)$	1336	1.889
Crystal size (mm ³)	0.60 x 0.25 x 0.02	0.08 x 0.07 x 0.03
Reflections collected/unique	9052/4732 [$R(int) = 0.0360$]	3200/2118 [$R(int) = 0.0287$]
Reflections with $[I > 2\sigma(I)]$	2954	1862
Data/restraints/ parameters	4732 / 267 / 464	2118 / 0 / 179
GOF on F^2	0.999	1.011
R_1, wR_2 [$I > 2\sigma(I)$]	0.0576, 0.1265	0.0588, 0.1465
R_1, wR_2 (all data)	0.1047, 0.1506	0.0688, 0.1582

Selected geometric parameters for **1** and **2** are given in Tables 2 and 3.

Compound $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**1**) crystallizes in the monoclinic centrosymmetric $P2_1/c$ (No.14) space group and its crystal structure consists of mononuclear $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation (Figure 1) and two ClO_4^- anions.

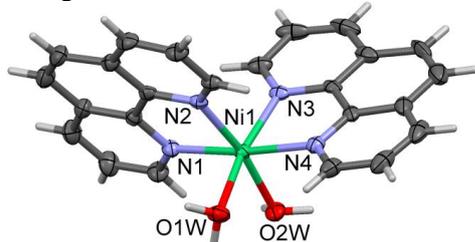


Figure 1. ORTEP view of the molecular structure of mononuclear $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ cation with partial atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

The nickel(II) ion displays a distorted octahedral coordination involving four nitrogen atoms of the chelating phen ligands and two oxygen atoms of water molecules coordinated in *cis* positions. The Ni–N distances are in the range of 2.069(3)–2.089(4) Å, and Ni–O distances are 2.084(3) and 2.103(3) Å. The twisted shape of the complex cation in **1** is characterized by the dihedral angle between the chelate phen ligands of 73.36°. Our survey of the Cambridge Crystallographic Data Base (ConQuest Version 1.19, CSD version 5.38) [12] reveals that the cation complex structure of **1** was found in several (20 hits) previously reported Ni(II) complexes with a similar coordination geometry. The structure of $[\text{Ni}(\text{phen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 0.4\text{H}_2\text{O}$ [13] differing only with 0.4 water molecules and synthetic mode preparation has been already described.

Table 2

Selected bond distances (Å) and angles (°) in metal coordination cores in compounds **1** and **2**.

1			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)-N(1)	2.070(4)	Ni(1)-N(4)	2.089(4)
Ni(1)-N(2)	2.069(3)	Ni(1)-O(1W)	2.084(3)
Ni(1)-N(3)	2.087(4)	Ni(1)-O(2W)	2.103(3)
Angle	<i>ω</i> , deg	Angle	<i>ω</i> , deg
N(2)-Ni(1)-N(1)	80.05(14)	O(1W)-Ni(1)-N(4)	91.68(15)
N(2)-Ni(1)-O(1W)	87.04(14)	N(3)-Ni(1)-N(4)	79.25(16)
N(1)-Ni(1)-O(1W)	94.99(15)	N(2)-Ni(1)-O(2W)	170.03(13)
N(2)-Ni(1)-N(3)	97.98(13)	N(1)-Ni(1)-O(2W)	93.99(14)
N(1)-Ni(1)-N(3)	94.29(15)	O(1W)-Ni(1)-O(2W)	85.53(14)
O(1W)-Ni(1)-N(3)	170.09(14)	N(3)-Ni(1)-O(2W)	90.39(13)
N(2)-Ni(1)-N(4)	97.40(14)	N(4)-Ni(1)-O(2W)	89.45(13)
N(1)-Ni(1)-N(4)	172.72(16)		
2			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Cd(1)-N(1)	2.306(5)	Cd(1)-O(1)	2.450(5)
Cd(1)-N(2)	2.334(5)		
Angle	<i>ω</i> , deg	Angle	<i>ω</i> , deg
N(1)-Cd(1)-N(1) ^{<i>i</i>}	180.0	N(2)-Cd(1)-O(1) ^{<i>i</i>}	92.22(19)
N(1)-Cd(1)-N(2) ^{<i>i</i>}	107.20(17)	N(1)-Cd(1)-O(1)	92.16(18)
N(1)-Cd(1)-N(2)	72.80(17)	N(2)-Cd(1)-O(1)	87.78(18)
N(2) ^{<i>i</i>} -Cd(1)-N(2)	180.0(2)	O(1) ^{<i>i</i>} -Cd(1)-O(1)	180.0
N(1)-Cd(1)-O(1) ^{<i>i</i>}	87.84(18)		

Symmetry transformations used to generate equivalent atoms: ^{*i*}-*x*+1, -*y*+1, -*z*+2.

Table 3

Hydrogen bond distances (Å) and angles (°) in compound **1**.

<i>D</i> - <i>H</i> ... <i>A</i>	<i>d</i> (<i>H</i> ... <i>A</i>)	<i>d</i> (<i>D</i> ... <i>A</i>)	∠(<i>DHA</i>)	Symmetry transformations for acceptor
O(1w)-H(1w1)···O(1)	1.82	2.683(17)	165.7	<i>x</i> , <i>y</i> , <i>z</i>
O(1w)-H(1w1)···O(4A)	1.94	2.750(7)	152.1	<i>x</i> , <i>y</i> , <i>z</i>
O(1w)-H(2w1)···O(4)	1.82	2.699(16)	178.5	- <i>x</i> +1, <i>y</i> -1/2, - <i>z</i> +1/2
O(1w)-H(2w1)···O(1A)	2.00	2.741(8)	141.7	- <i>x</i> +1, <i>y</i> -1/2, - <i>z</i> +1/2
O(2w)-H(1w2)···O(6A)	2.07	2.890(14)	157.8	- <i>x</i> +1, <i>y</i> -1/2, - <i>z</i> +1/2
O(2w)-H(2w2)···O(3)	2.27	2.738(18)	114.1	- <i>x</i> +1, <i>y</i> +1/2, - <i>z</i> +1/2

Intermolecular $\text{OH}\cdots\text{O}(\text{ClO}_4^-)$ hydrogen bonds involving the coordinating water molecules as donors and the perchlorate O atoms as acceptors form zigzag-like hydrogen-bonding chains (Figure 2(a), Table 3), which are further assembled *via* π - π stacking interactions between adjacent phen rings, thus forming a supramolecular network structure. Two mononuclear cations related by inversion center are combined into centrosymmetric dimers *via* stacking interactions involving phen ligands by

overlapping of the phenyl-phenyl (centroid-to-centroid distance is 3.706 Å) and pyridine-phenyl rings (centroid-to-centroid distance is 4.002 Å), and these dimers are further linked into an infinite supramolecular polymer through longer π - π stacking interaction between pyridine-pyridine rings (centroid-to-centroid distance is 4.069 Å) of phen ligands (Figure 2(b), (c); Table 4). The Ni \cdots Ni separations through the stacked ligands between neighbouring complexes are 9.190 and 9.975 Å.

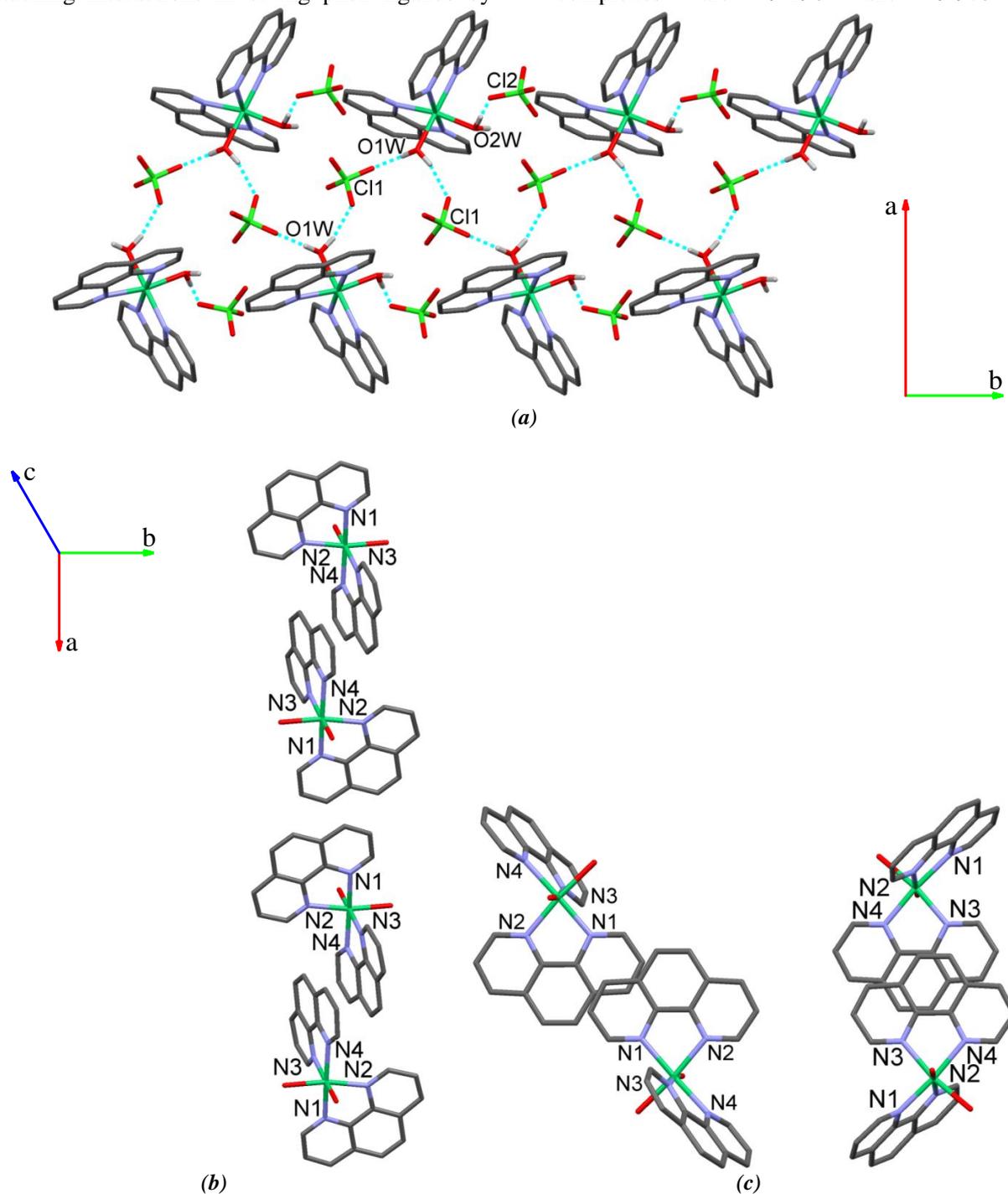


Figure 2. (a) The fragment of 1D hydrogen-bonding chain in 1.

(b) Tape of the cation complexes supported by π - π stacking interactions along the *a* axis.

(c) Two modes of phen overlapping; view perpendicular to the plane of the overlapping phen ligands.

Compound **2**, with the composition $[\text{Cd}(\text{ClO}_4)_2(\text{phen})_2]$, crystallizes in the triclinic *P*-1 (No.2) space group. The mononuclear unit resides on the inversion centre and its structure is shown in Figure 3(a). The cadmium atom is coordinated by four nitrogen atoms of two chelating phen group and two oxygen atoms from monodentate perchlorate anions to form a distorted N_4O_2 -octahedral surrounding. In the equatorial platform, the Cd–N bonds are equal to 2.306(5) and 2.334(5) Å, and the apical Cd–O bonds are equal to 2.450(5) Å (Table 2). The ClO_4^- anions are arranged above and below the equatorial plane of the complex. It might be emphasized that a similar situation of metal cations in N_4 phen equatorial plane has been documented for 7 transition metal coordination compounds, 3 of them are Cd(II)

compounds: mononuclear bis(1H-benzotriazole-7-sulfonato)-bis(1,10-phenanthroline)-cadmium dihydrate compound [14] and two coordination polymers *catena*-((μ_2 -naphthalene-1,5-disulfonato)-bis(1,10-phenanthroline)-cadmium) [15] and *catena*-[bis(μ -dihydrogen benzene-1,2,3,5-tetracarboxylato)-diaqua-tetrakis(1,10-phenanthroline)-tri-cadmium(II) dinitrate] [16].

Only one type of π - π stacking interactions was registered in **2**, between neighbouring pyridine-pyridine rings of hydrophobic phen molecules of mononuclear compound (centroid-to-centroid distance equal to 3.753 Å), yielding one-dimensional supramolecular ladder-like chains along the *c* direction (Figure 3(b), Table 4). The Cd...Cd separation through the stacked ligands between neighbouring complexes is 9.443 Å.

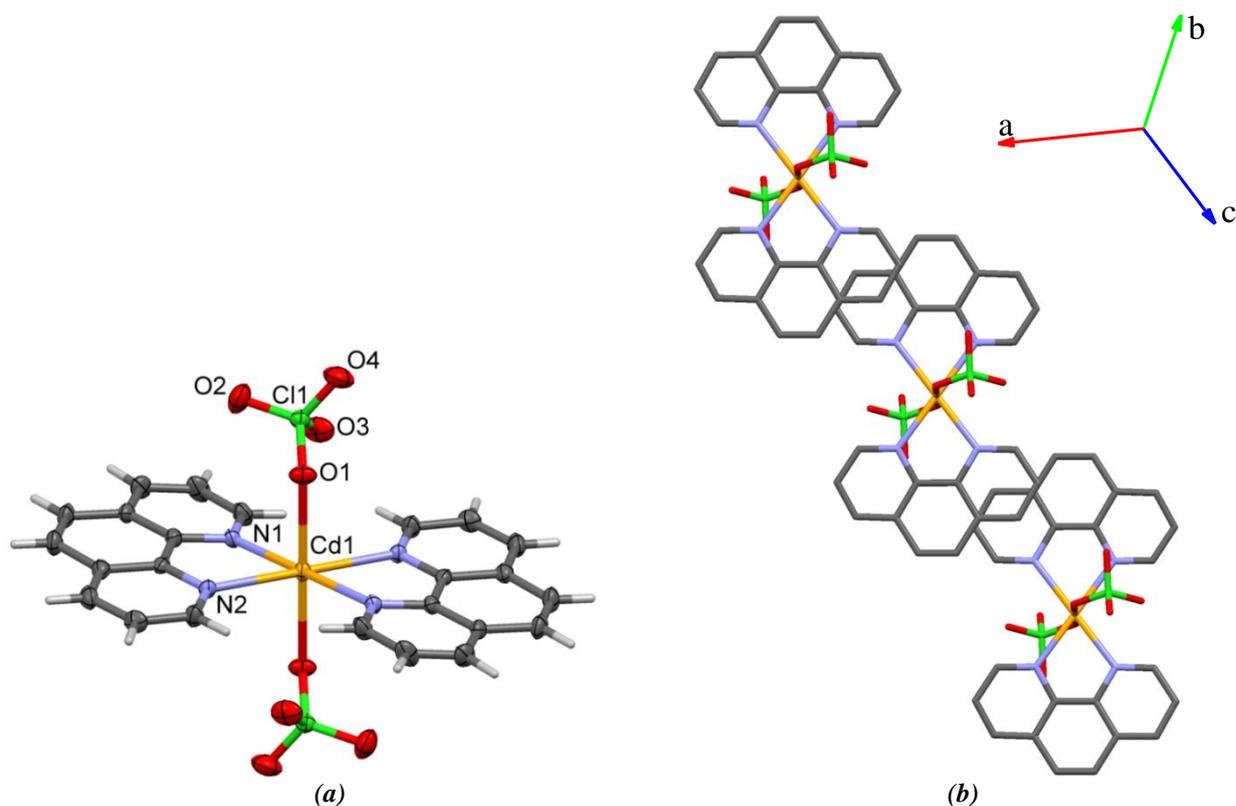


Figure 3. (a) ORTEP view of the molecular structure of mononuclear compound in **2** with partial atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

(b) Tape of the complexes supported by π - π stacking interactions; view perpendicular to the plane of the overlapping phen ligands.

Luminescent properties

The luminescence properties of complexes **1** and **2** as well as pure phen ligand were studied in the solid state at room temperature, $\lambda_{ex} = 337$ nm (Figure 4). The free phen ligand fluorescence spectrum exhibits two intensive bands at 2.95 eV (420 nm) and at 2.8 eV (443 nm), and a little one at 1.85 eV (670 nm) (Figure 4), the presence of which can be assigned to ligand chromophore

moieties. The corresponding Ni(II) and Cd(II) complexes present different emission peak ratios that create different colours. Compound **1** emits blue-green fluorescence with characteristic sharp emission peaks at 3.25 eV (381 nm), 2.50 eV (495 nm) and 1.85 eV (670 nm), while monomeric complex **2** gives white-light emission with characteristic emission peaks at 3.20 eV (387 nm), 2.95 eV (420 nm) and 2.40 eV

(516 nm). The same blue-shift emission was registered for the coordination compound with a similar composition $[\text{Cd}(\text{Hpac})(\text{phen})_2]\text{ClO}_4$ (where Hpac=pyrazole-3-carboxylic acid) [17]. The authors explain that the emission bands in their spectrum come from a mixed ligand charge transition combining with a perchlorate-phen charge transition.

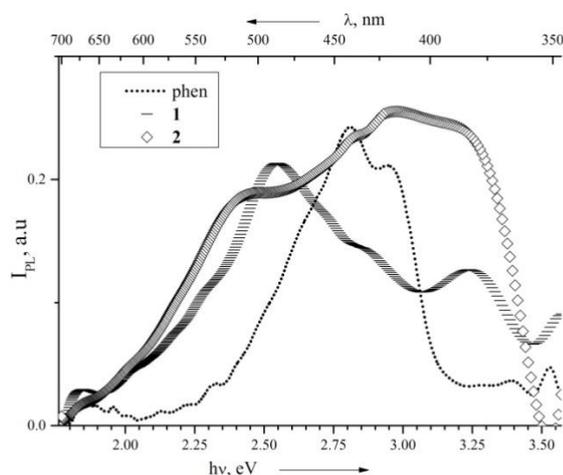


Figure 4. Solid-state luminescence emission spectra of compounds 1 and 2, as well as free phen ligand.

Conclusions

In summary, we have synthesized two bis-phenanthroline mononuclear complexes of Ni(II) and Cd(II) along with perchlorate counter ions. The smaller nickel(II) ion forms a *cis* complex with outer-sphere perchlorates, while the cadmium(II) ion forms a *trans* complex involving inner-sphere perchlorate ligands. Crystal packing in **1** reveals supramolecular 3D architecture governed by combination of OH...O hydrogen bonds and stacking interactions between the planar adjacent phen fragments, while in **2** the crystal packing is managed exclusively through π - π stacking interactions between neighbouring pyridine rings of hydrophobic phen molecules, yielding one-dimensional supramolecular ladder-like chains. Compounds **1** and **2** reveal intraligand-based luminescent properties.

Acknowledgments

Ecaterina Tocana and Lilia Croitor thank the Grant for Young Scientists (16.80012.02.05F) for financial support.

References

- Salonen, L.M.; Ellermann, M.; Diederich, F. Aromatic rings in chemical and biological recognition: energetics and structures. *Angewandte Chemie International Edition*, 2011, 50(21), pp. 4808–4842. DOI: [10.1002/anie.201007560](https://doi.org/10.1002/anie.201007560).
- Capello, M.C.; Hernández, F.J.; Broquier, M.; Dedonder-Lardeux, C.; Jouvet, C.; Pino, G.A. Hydrogen bond vs. π -stacking interactions in the *p*-aminophenol...*p*-cresol dimer: an experimental and theoretical study. *Physical Chemistry Chemical Physics*, 2016, 18(45), pp. 31260-31267. DOI: [10.1039/C6CP06352G](https://doi.org/10.1039/C6CP06352G).
- Wang, Q.; Li, Z.; Tao, D.-D.; Zhang, Q.; Zhang, P.; Guo, D.-P.; Jiang, Y.-B. Supramolecular aggregates as sensory ensembles. *Chemical Communications*, 2016, 52, pp. 12929-12939. DOI: [10.1039/C6CC06075G](https://doi.org/10.1039/C6CC06075G).
- Černý, J.; Hobza, P. Non-covalent interactions in biomacromolecules. *Physical Chemistry Chemical Physics*, 2007, 9(39), pp. 5291–5303. DOI: [10.1039/B704781A](https://doi.org/10.1039/B704781A).
- Wilson, K.A.; Wetmore, S.D. Combining crystallographic and quantum chemical data to understand DNA-protein π -interactions in nature. *Structural Chemistry*, 2017, 28(5), pp 1487–1500. DOI: <https://doi.org/10.1007/s11224-017-0954-7>.
- Melnic, E.; Tocana, E.; Siminel, A.V.; Croitor, L. Supramolecular solid-state patterns generated by hydrogen bonding and π - π stacking interactions in the mononuclear Cr(III) complexes. *Polyhedron*, 2015, 102, pp. 410–416. DOI: <https://doi.org/10.1016/j.poly.2015.09.069>.
- Cadmium salts are carcinogenic and toxic: Cadmium in the environment and its significance to man: an inter-departmental report. (Pollution paper No17), Her Majesty's Stationery Office, London, 1980, 64 p. <http://trove.nla.gov.au/work/25996390>.
- Sheldrick, G.M. A short history of SHELX. *Acta Crystallographica*, 2008, A64, pp. 112-122. DOI: <https://doi.org/10.1107/S0108767307043930>.
- Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallographica*, 2015, C71, pp. 3-8. DOI: <https://doi.org/10.1107/S2053229614024218>.
- Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: visualization and analysis of crystal structures. *Journal of Applied Crystallography*, 2006, 39, pp. 453-457. DOI: <https://doi.org/10.1107/S002188980600731X>.
- Abdel-Rahman, L.; Battaglia, L.P.; Rizzoli, C.; Sgarabotto, P. Synthesis, characterization, and X-ray crystal structure of tris(1,10-phenanthroline) nickel(II) perchlorate hemihydrate. *Journal of Chemical Crystallography*, 1995, 25(10), pp. 629-632. DOI: <https://doi.org/10.1007/BF01665968>.
- Groom, C.R.; Bruno, I.J.; Lightfoot, M.P.; Ward, S.C. The Cambridge structural database. *Acta Crystallographica*, 2016, B72, pp. 171–179. DOI: <https://doi.org/10.1107/S2052520616003954>.
- Tang, X.-Y.; Qiu, Y.-C.; Sun, F.; Yue, S.-T. Diaquabis(1,10-phenanthroline-*k*²*N,N'*)nickel(II)

- diperchlorate 0.4-hydrate. *Acta Crystallographica*, 2007, E63, m2515.
DOI: <https://doi.org/10.1107/S1600536807043565>.
14. Zhu, X.-H.; Cheng, X.-C. Bis(1*H*-benzotriazole-7-sulfonato-*kO*)bis-(1,10-phenanthroline-*k²N,N'*) cadmium dihydrate. *Acta Crystallographica*, 2011, E67, m1698.
DOI: <https://doi.org/10.1107/S1600536811045971>.
15. Zhu, Y.; Shao, Sh.; Ma, K.; Zhao, H.; Qiu Y. Syntheses, structures, and photoluminescence properties of Zn(II)/Cd(II) supramolecular architectures based on 1,5-naphthalenedisulfonate and 1,10-phenanthroline ligands. *Monatshefte für Chemie*, 2013, 144(10), pp 1507–1512.
DOI: <https://doi.org/10.1007/s00706-013-1037-0>.
16. Xia, Ch.-K.; Wu, F.; Yang, K.; Sun, W.; Min, Y.-Y.; Wu, Y.-L.; Lu, X.-J. Zn(II) and Cd(II) complexes assembled from versatile 1,2,3,5-benzenetetracarboxylic acid and chelating N-donor auxiliary coligands. *Polyhedron*, 2016, 117, pp. 637–643.
DOI: <https://doi.org/10.1016/j.poly.2016.07.003>.
17. Liu, G.-N.; Zhu, W.-J.; Chu, Y.-N. ; Li, C. Three d¹⁰ metal coordination compounds based on pyrazole-3-carboxylic acid showing mixed-ligand characteristic: Syntheses, crystal structures, and photoluminescent properties. *Inorganica Chimica Acta*, 2015, 425, pp. 28–35.
DOI: <https://doi.org/10.1016/j.ica.2014.10.024>.