



Synthesis, crystal structures and luminescence properties of new multi-component co-crystals of isostructural Co(II) and Zn(II) complexes

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ABSTRACT

Two novel isostructural compounds containing multi-component co-crystals $[M(C_6H_4NO_2)_2 \cdot (H_2O)_2] \cdot (C_9H_6O_6)_2$ ($M = Co$ (**1**), Zn (**2**), $C_6H_4NO_2$ = Picolinic acid, $C_9H_6O_6$ = Trimesic acid) have been synthesized. The compounds were characterized by elemental analysis, FT-IR, UV–Visible and 1H NMR spectroscopies as well as thermal and single crystal X-ray diffraction analyses. Single crystal X-ray diffraction analysis reveals that **1** and **2** are isostructural. Compound **1** crystallizes in triclinic space group (*P*-1, with $a = 5.154$ (10) Å, $b = 11.125$ (2) Å, $c = 14.113$ (3) Å, $\alpha = 91.01$ (3)°, $\beta = 100.54$ (3)°, and $\gamma = 102.71$ (3)°). In a similar fashion, compound **2** crystallizes in triclinic space group (*P*-1, with $a = 5.1735$ (3) Å, $b = 11.0930$ (10) Å, $c = 14.1554$ (8) Å, $\alpha = 91.70$ (3)°, $\beta = 100.26$ (3)°, $\gamma = 102.90$ (3)°). The metal (II) cation presents distorted MN_2O_4 octahedral geometry with H_2O molecules coordinated to the metal in equatorial position while the picolinic acid molecules are axially coordinated through the pyridine *N* atom. The two trimesic acid molecules are not part of the first coordination sphere. Compounds **1** and **2** constitute an example of a class of coordination compound of multicomponent crystals having trimesic acid outside the coordination sphere where it is neither protonated or deprotonated. The two compounds were investigated for luminescence properties.

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1. Introduction

In recent years, several disciplines such as crystal engineering, material chemistry, metallurgy, polymer chemistry and solid state chemistry have developed from the pursuit of practical and innovative multicomponent solids (co-crystal). A co-crystal is a crystalline structure composed of at least two components, where the components may be atoms, ions or molecules [1–4]. Co-crystal engineering has attracted great interest not only because of its unique properties, but also its wide pharmaceutical [5,6] and industrial applications such as in production of energetic materials [7]. Therefore, the design and synthesis of new molecular solids

(co-crystals) are important because they could serve as raw material for industrial production.

Carboxylic and phenolic acids are strong candidates employed in producing co-crystals due to the presence of multiple hydrogen bond donors and acceptors that enable them to form a stable and diverse range of supramolecular synthons. Many supramolecular synthons composed of carboxylic acid dimers [8], carboxylic acid–basic nitrogen [9,10], carboxylic acid–amides [11,12] and phenol–carboxylates [13] are self-complementary and can also engage in robust and reliable supramolecular heterosynthons with complementary functional groups. Many carboxylic acids like 3-chlorobenzoic acid, ferulic acid, gallic acid, picolinic acid and trimesic acid *etc.* [14] are very useful ligands for this purpose. Trimesic acid (benzene-1,3,5-tricarboxylic acid) is widely used in synthetic reactions and as a component in co-crystals and coordination complexes. Pyridine-2-carboxylic acid and its derivatives exist in

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nature and are widely used in medicinal chemistry due to their variety of physiological properties [15,16]. Picolinic acid is an endogenous metabolite of L-tryptophan (TRP) that has been reported to possess a wide range of medicinal values [15,17]. A good number of picolinic acid and its metal complexes synthesized using solvent-based synthesis have been reported to possess a wide range of neuro-protective, immunological, therapeutic and anti-proliferative effects within the body [15,18–22]. The picolinate ligand is able to chelate metal ions and can display widely varying coordination modes as a multidentate ligand. It is the most efficient chelator for metal ions such as chromium, cobalt, copper, manganese, molybdenum, iron and zinc in body fluids [23]. Generally, transition metal ions are Lewis acids being electron deficient, while carboxylic acids are Lewis base which are electron rich. The attraction between positive charge on the metal (M^{2+}) and the negative charge on the carboxylic group (COO^-) leads to the formation of metal-complexes [24]. In addition, both picolinic and trimesic acid (Fig. S1) show extrinsic luminescent property because of the availability of conjugation in their molecular structures. The multi-component co-crystal formed by coordinating any d^{10} metal ion (e.g. Zn) with picolinate and trimesate ion also exhibit characteristic luminescence property [25]. Luminescent materials can be prepared by reaction of d-metal ion (diamagnetic) with fluorescence active ligands because of their potential applications as fluorescent sensors or in light-emitting devices [26–30].

Recently, we reported a series of coordination compounds constructed from picolinic acid [15]. Solid-state exposure of one of the compounds with Co(II) as the metal ion displayed a selective and irreversible colour change towards some common organic solvents, thereby functioning as sensors for these solvents. In continuation of our research into metal (II) complexes of carboxylic acids, we hereby report the synthesis, crystal structure and luminescence properties of novel multi-component co-crystals of coordination compounds.

2. Experimental section

2.1. Materials and methods

All reagents and solvents were of analytical grade and were used without further purification. High purity picolinic acid, trimesic acid, $CoSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot H_2O$ were commercially obtained from Sigma-Aldrich. The melting points were determined on MPA100 Optimelt Automated Melting Point System. Elemental analyses (C, H and N) were performed by standard methods on a Carlo Erba Model EA1108 elemental analyzer at micro analytical laboratory of Medac Limited UK. FT-IR spectra in the range of 4000–400 cm^{-1} were obtained from samples using KBr pellets on FTIR-8501 Shimadzu Spectrometer. The thermo-gravimetric analyses (TGA) were carried out on a TGA Q500 V6.7 Build 203 instrument under a nitrogen atmosphere at a heating rate of 10 $^{\circ}C\ min^{-1}$ from room temperature up to a temperature of 600 $^{\circ}C$. UV–Vis Electronic spectra of the complexes were recorded on a Shimadzu UV 3100spectrophotometer. Fluorescence measurements were obtained on a Perkin Elmer LS45 Fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length. The fluorescence properties of the ligands (picolinic acid and trimesic acid) and their resulting Co(II) and Zn(II) complexes were recorded at room temperature using DMSO as solvent.

2.2. Crystallographic data collection and structural analysis

For compounds **1** and **2**, single crystals suitable for X-ray crystallography were obtained by slow evaporation of aqueous/ethanolic solution. Single crystal X-ray intensity data collections were

performed on a Bruker Kappa Apex II Duo diffractometer (Madison, Wisconsin) with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073\ \text{\AA}$). Cryoloops were used to mount crystals under Paratone oil (Exxon Chemical Company, Houston, Texas). Unit cell data were initially recorded at 294 (2) K to ensure that no phase changes occurred on cooling to the data collection temperature of 173 (2) K, the latter being achieved with a Cryostream cooler (Oxford Cryosystems, Oxford, UK). Program SAINT [31] was used for data reduction and multi-scan absorption corrections were applied with SADABS [32]. The X-seed interface [33] was used to operate the SHELX suite of programs [34] to solve the structures by direct methods and refine them by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, while hydrogens were included in idealized positions in a riding model with isotropic thermal parameters in the range 1.2–1.5 times those of their parent atoms. Details of the crystal parameters, data collection and refinements are listed in Table 1. Table 2 lists selected molecular parameters.

2.3. Synthesis of the complexes **1** and **2**

2.3.1. Synthesis of $[Co(C_6H_4NO_2)_2(H_2O)_2](C_9H_6O_6)_2$ (**1**)

Compound **1** was synthesized by mixing a solution of trimesic acid (0.210 g, 1 mmol) in ethanol (10 ml), a solution of picolinic acid (0.246 g, 2 mmol) in ethanol (10 ml) and a solution of $CoSO_4 \cdot 7H_2O$ (0.281 g, 1 mmol) in water (10 ml). The mixture was stirred at room temperature for 2 h. A clear solution was obtained and left standing for slow evaporation at room temperature (Scheme 1). Pink coloured crystals suitable for X-ray crystallographic analysis were obtained after two weeks. The pink crystals were filtered and washed with mixture of water and ethanol in the ratio 1:2 and dried at room temperature. Yield: 52.0%, M.wt: 759.44 $gmol^{-1}$, M. pt: 240 $^{\circ}C$, Anal. Calc for $C_{30}H_{24}CoN_2O_{18}$ (%): C 47.40; H 3.16; N 3.69; Found %: C, 47.40; H, 3.14; N, 3.68. IR (KBr pellet, cm^{-1}) 3470, 1707, 1678, 1597, 1392, 1320, 675, 609, 513, 455.

2.3.2. Synthesis of $[Zn(C_6H_4NO_2)_2(H_2O)_2](C_9H_6O_6)_2$ (**2**)

Complex **2** was obtained by a similar method as described for **1** using $ZnSO_4 \cdot H_2O$ (0.180 g, 1 mmol) in place of cobalt (II) sulfate. The product was obtained as white crystals. Yield: M.wt: 767.37 $gmol^{-1}$, Yield: 75.7%, M. pt: 230 $^{\circ}C$, Anal. Calc for $C_{30}H_{24}ZnN_2O_{18}$ (%): C

Table 1
Crystal data and structure refinement for **1** and **2**.

Compound reference	1	2
Empirical formula	$C_{30}H_{24}CoN_2O_{18}$	$C_{30}H_{24}ZnN_2O_{18}$
Formula weight	759.44	767.37
Temperature/K	173	173
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/ $\text{\AA}$	5.1459 (10)	5.1735 (3)
b/ $\text{\AA}$	11.125 (2)	11.093 (10)
c/ $\text{\AA}$	14.113 (3)	4.1554 (3)
$\alpha/^\circ$	91.61 (3)	91.696 (3)
$\beta/^\circ$	100.540 (3)	100.259 (3)
$\gamma/^\circ$	102.710 (3)	102.908 (3)
Volume/ $\text{\AA}^3$	772.9 (3)	777.14 (9)
Z	1	1
$\rho_{\text{calc}}\ mg/mm^3$	1.632	1.636
μ/mm^{-1}	0.646	0.881
F (000)	389	392
Goodness-of-fit on F^2	0.902	0.857
Data/restraints/parameters	3694/0/235	3542/5/247
Index ranges (h,k,l)	$\pm 6, \pm 14, \pm 18$	$\pm 6, \pm 14, \pm 18$
R_1 [$I > 2\sigma(I)$]	0.0496	0.0271
wR_2 (all data)	0.1701	0.0821
Max/min ($e\ \text{\AA}^{-3}$)	0.652 and -0.911	0.608 and -0.849

Table 2
Interatomic bond distances (Å) and angles (°) of **1** and **2**.

Bond Lengths (Å)	1	2	Bond Angles (°)	1	2
M1–O2	2.092	2.124	O2–M1–N3	94.04	94.31
M1–N3	2.128	2.112	O2–M1–O10	92.38	93.16
M1–O10	2.074	2.091	N3–M1–N3	180.0	180.0

46.91; H 3.13; N 3.65; Found %: C, 46.91; H, 3.12; N, 3.66. IR (KBr pellet, cm^{-1}) 3483, 1707, 1678, 1597, 1392, 1320, 675, 609, 513, 457; ^1H NMR ($\text{DMSO}-d_6$): δ/ppm = 4.38 (s, 4H, H–O–H), 7.63 (d, 2H, Ar–H, J = 7.50 Hz), 8.30 (d, 2H, Ar–H), 8.56 (m, 4H, Ar–H, J = 7.50 Hz), 8.86 (s, 3H, Ar–H, J = 1.50 Hz), 13.08 (s, 3H, OH).

3. Results and discussions

The chemical reaction of picolinic acid and trimesic acid with the sulfate salt of Co(II) and Zn(II) at room temperature, led to the formation of two multi-component co-crystals. The compounds are soluble in DMSO, DMF and warm water, but insoluble in other common organic solvents such as acetone, ethanol and methanol. The elemental analyses of the two compounds agreed with the stoichiometry $[\text{M}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2](\text{C}_9\text{H}_6\text{O}_6)_2$. Determination of stoichiometric ratio using Job's method revealed a mole ratio of 1:2:2 metal to each of the ligands.

The position of the asymmetric ν_{as} (COO^-) and symmetric ν_{s} (COO^-) bands of the picolinic acid carboxylate groups in the FT-IR spectra of **1** and **2** suggests a unidentate bonding mode for the carboxylic groups in the complexes [35]. The FT-IR also revealed that the coordination of the picolinate ligand to the metals is through the carboxylate oxygen and the nitrogen atom of the pyridine ring and that the trimesic acid did not coordinate to the metals but lies outside the coordination sphere [36]. The IR spectra of both compounds showed similar features, an indication that the two compounds are isostructural (Fig. S2).

3.1. Thermal analysis of **1**

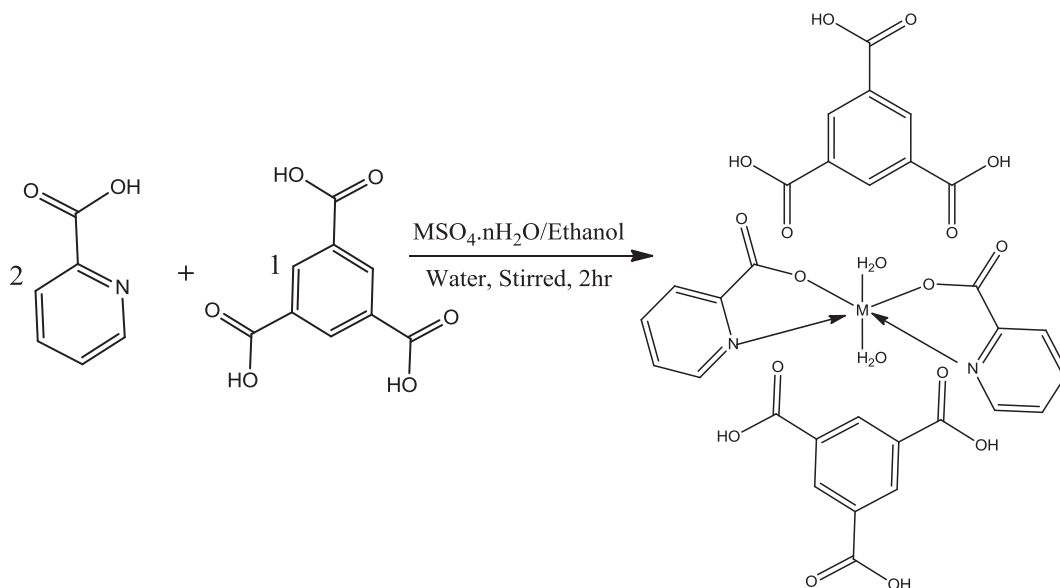
The thermogravimetric-differential thermal analysis (TG-DTA) profiles of compound **1** is shown in Fig. 1a. The compound was

thermally stable up to around 200 °C where the first mass loss was observed. In this first step of thermal decomposition, the compound shows weight loss corresponding to two coordinated water molecules (calcd./found: 4.74/4.8%) [33]. The second thermal decomposition stage follows between 245 and 350 °C which is attributed to the loss of the two uncoordinated trimesic acid molecules (calcd./found: 55.41/54.10%). The third thermal decomposition between 420 and 510 °C, shows weight loss corresponding to the remaining coordinated picolinate molecules (calcd./found: 32.42/31.00%) [33]. The TG-DTA decomposition profiles of compound **2** as shown in Fig. 1b revealed that the decomposition of the two compounds follows similar pattern. The first weight loss at around 175 °C corresponds to a loss of two coordinated water molecules (calcd./found: 4.7/4.9%). After the release of the water molecules, the second decomposition steps occurred at a higher temperature range than in **1** between 280 and 385 °C which can be ascribed to the loss of the two uncoordinated trimesic acid molecules (calcd./found: 54.84/52.5%). The final decomposition step involves the release of the two coordinated picolinate ligands between 425 and 480 °C (calcd./found: 32.08/28.80%).

3.2. Description of the crystal structure of compounds **1** and **2**

The ORTEP diagram of the structures of $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2](\text{C}_9\text{H}_6\text{O}_6)_2$ (**1**) and $[\text{Zn}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2](\text{C}_9\text{H}_6\text{O}_6)_2$ (**2**) are shown in Figs. 2 and 3 while the selected interatomic bond distances and angles around M (II) are presented in Table 2. The two compounds crystallize in a triclinic space group P-1 in which the metal cation is in octahedral environment. The Zn(II) and Co(II) ions are equatorially coordinated to two molecules of picolinate through the carboxylate O and the pyridine N atom, axially coordinated to two molecules of water and also have two trimesic acid molecules which are outside the coordination sphere. The crystallographic data and the structure refinement parameters of the two compounds show similar features confirming that they are isostructural.

The Co–O distances [2.092 and 2.074 Å] are comparable to those found in $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ [22]. Similarly, the Co(1)–N (3) distance (2.128 Å) is in good agreement with the value found in $[\text{Co}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ [22]. In the co-crystal, the bond



Scheme 1. Synthesis of compounds **1** and **2**; Compound **1**: M = Co, n = 7; Compound **2**: M = Zn, n = 1.

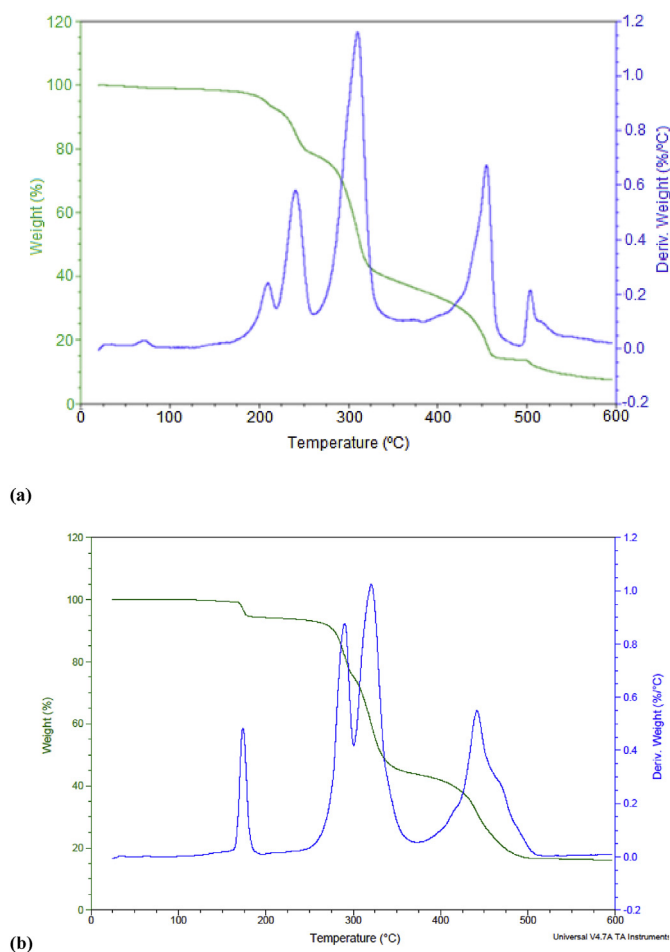


Fig. 1. The TGA curves for **1** and **2**.

distance of Co(1)–O (10) is slightly shorter than the bond distance of Co(1)–N (3) and Co(1)–O (2), this indicates that the coordination ability of O (oxygen) atom of the water molecule is stronger than the N (nitrogen) atom of the pyridine ring and O (oxygen) atom of the carboxyl. The bond angles O (2)–Co(1)–O (10) and O (2)¹–Co(1)–O (10)¹ are 92.38°; O (2)–O (1)–N (3) and O (2)¹–Co(1)–N (3)¹ are 94.04°; while N (3)–Co(1)–N (3) and N (3)¹–Co(1)–N (3)¹ are 180

which are comparable to other cobalt (II) picolinate complexes [22]. In the structure of this compound, the molecules of the co-crystals are held together via strong intermolecular hydrogen bond.

The crystal structure of compound **2** is similar to that of **1** with the Zn (II) ion octahedrally bonded to two picolinate through N– and O– atoms and two water molecules. The Zn–O (Zn1–O2 = 2.124 Å, Zn–O10 = 2.091 Å) bond lengths are similar while the Zn–N (Zn–N3 = 2.112 Å) bond lengths is slightly longer than the Zn–O distance. These values are similar to those reported in the literature for Zn(II)-picolinate complexes [23,37–39].

In the co-crystal, the bond distance of Zn (1)–O (10) is slightly shorter than the bond distance of Zn (1)–N (3) and Zn (1)–O (2), this indicates that the coordination ability of O (oxygen) atom of the water molecule is stronger than the N (nitrogen) atom of the pyridine ring and O (oxygen) atom of the carboxyl as observed in **1**. The bond angles O (2)–Zn (1)–O (10) and O (2)¹–Zn (1)–O (10)¹ are 93.16°; O (2)–Zn (1)–N (3) and O (2)¹–Zn (1)–N (3)¹ are 94.31°; while N (3)–Zn (1)–N (3) and N (3)¹–Zn (1)–N (3)¹ are 180 which are comparable to other Zn (II) picolinate complexes [37–39]. The molecules of the co-crystals in this compound are also held together via strong intermolecular hydrogen bond in the same fashion as in **1** (Fig. 4).

While trimesic acid is frequently used as a coordinating ligand in coordination complexes, it is seldom reported as a non-coordinating, neutral component in co-crystals with coordination complexes. A survey of the CSD [version 5.38, updated May 2017] [40] shows that neutral trimesic acid has been reported as a component of crystal structures 143 times (excluding the structure of trimesic acid alone). Of these, it is only present seven times as a neutral non-coordinating component with a coordination complex as the other component in the crystal structure. Of these seven structures, refcodes AVELAO, BIMDOR, EXAGIT, HEVVUA, IKAJIN, LOFBAK, LOFBEO, the latter two are the most closely related to the structures reported here. LOFBAK is a co-crystal of trimesic acid with bis(2-pyridyl)amine-palladium (II) with a third component, a molecule of water. The structure is a clathrate, wherein the trimesic acid and water form large hydrogen-bonded rings, capturing the palladium complex within these large channels. LOFBEO consists of the same components, without the water, and packs in the same way, capturing the palladium complex as a “guest” in a trimesic acid hydrogen bonded channel. The packing of **1** and **2** also shows large hydrogen-bonded rings, but in this case, the coordination compound [M(2pic)₂(H₂O)₂] is part of the hydrogen-bonding system. The differences are illustrated in Fig. S5 for (a) **2** and (b) LOFBAK.

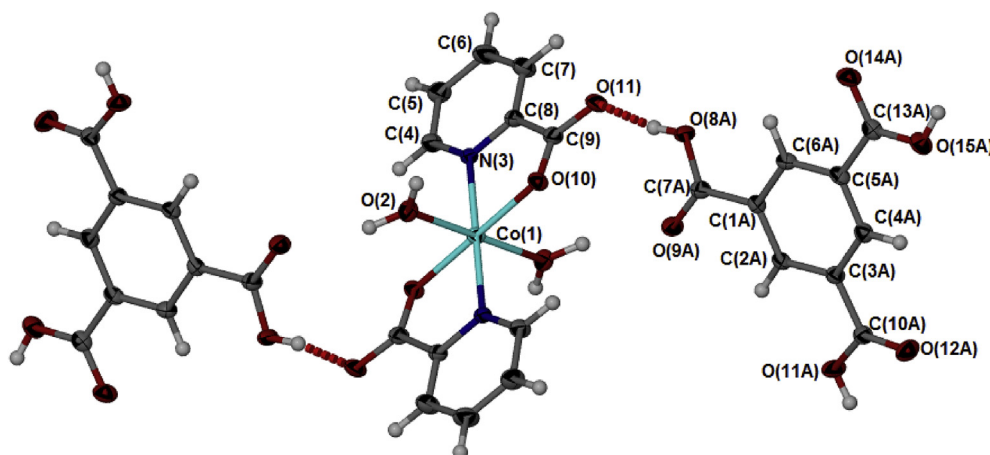


Fig. 2. ORTEP diagram of compound **1**.

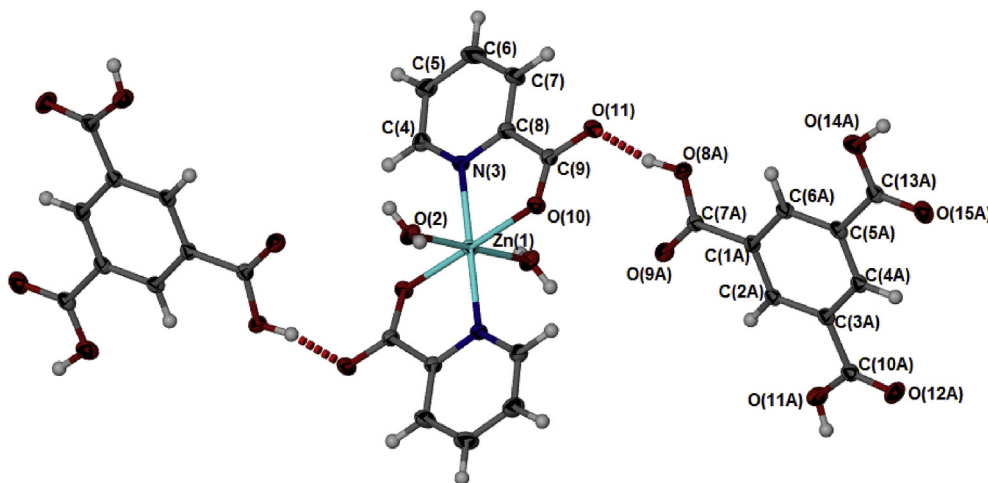


Fig. 3. ORTEP diagram of compound 2.

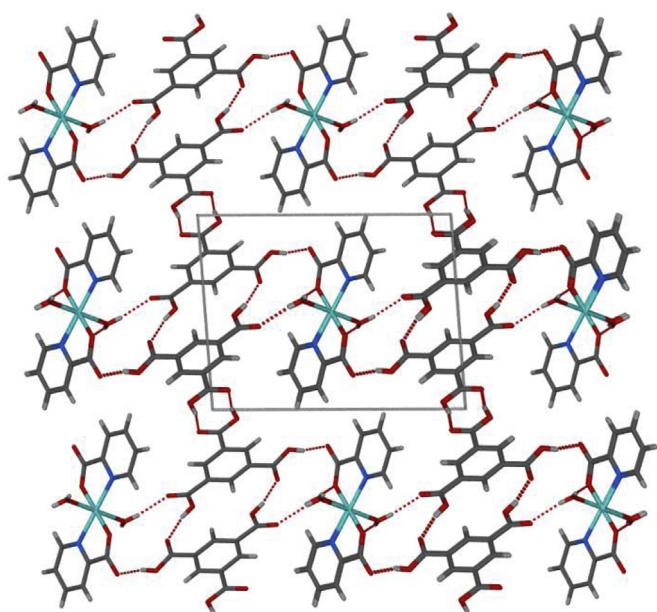


Fig. 4. Packing diagram, viewed down [100], of the crystal structure of 2.

3.3. Luminescence properties

The free ligands, picolinic and trimesic acids displayed luminescence properties at *ca* 449.2 nm and *ca* 380.9 nm respectively, (Fig. 5). The fluorescence emission spectrum of **1** and **2** are shown in Figs. 6 and 7 respectively. Complex **2** exhibited a strong luminescence properties at *ca* 388.7 nm with a shoulder at *ca* 407.8 nm attributed to trimesic acid, while complex **1** displayed no luminescence, the lack of luminescence properties may be attributed to Co(II) ion acting as a quenching agent [41]. The peaks around 586 nm for **2** may be ascribed to the intraligand emission ($\pi-\pi^*$) from the ligands [42]. The fluorescence intensity of complex **2** was observed to be larger than that of the free ligands, this is probably due to the rigidity of the coordinated ligand in these complexes in comparison to the free ligand [43]. The enhanced emission was observed as we move from amorphous solids (ligands) to crystal state which suggests that the crystallization of picolinic acid and trimesic acid with the Zn^{2+} boosted the emission in compound **2**.

The metal salt could be said to be interrupting the strong $\pi-\pi$ interactions between luminogens, picolinic acid [44]. The luminescent emission exhibited by complex **2** suggests that this complex may be a potential compound for optical and blue-light emitting materials.

3.4. Electronic spectral studies

The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the positions and number of $d-d$ transition peaks. The electronic absorption spectra of the ligands and its Co(II) and Zn(II) complexes were recorded at room temperature using DMF as solvent. An absorption band observed around 280 nm in trimesic acid was assigned to $n-\pi^*$ of the carbonyl group of the compound. Picolinic acid presented an absorption band at 261 nm which is characteristic of the enol group, while the adsorption bands for azomethine was not visible on the spectrum (Fig. S6). The absorption band 261 and 280 nm of the enol and carbonyl group chromophores $\pi-\pi^*$ and $n-\pi^*$ transitions are shifted compared to the ligand indicating the enolic oxygen, the imine nitrogen are involved in the coordination with Co(II) and Zn(II) ions. For Co(II) complex, the spectrum of the metal complex shows (inset of Fig. 8) that the absorption around 400–600 nm is due to ligand to metal charge transfer (LMCT) and $d-d^*$ transition band of the metal in the complex. The electronic spectra of Co(II) complex showed two spin-allowed transitions at 477 and 547 nm assignable to $4T1g(F) \rightarrow 4A2g(F)$ and $4T1g(F) \rightarrow 4T1g(P)$ transitions respectively, are in conformity with octahedral arrangements for Co(II) ion [45]. Zinc (II) complex does not exhibit $d-d$ electronic transition due to the filled d-orbital. The electronic spectrum of the Zn(II) complex shows an absorption band (shoulder) at 295 nm and is attributed to the LMCT transition (Fig. 9), which is compatible with this complex having an octahedral structure [46,47].

4. Conclusion

The study demonstrates that coordination of multicomponent crystals can be synthesized from reaction of metal salts with picolinic and trimesic acids. The spectroscopic and PXRD showed that **1** and **2** are isostructural; an example of multicomponent crystal coordination compounds where trimesic acid is not coordinated or deprotonated but outside the coordination. The fluorescence properties in solution were investigated, an enhanced

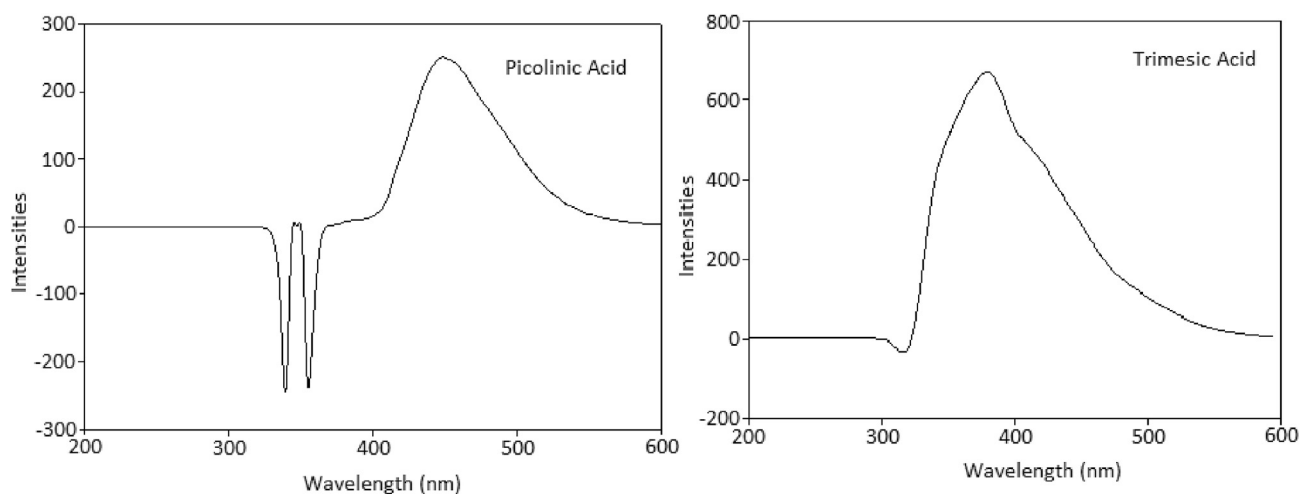


Fig. 5. Fluorescence spectrum of picolinic and trimesic acid at room temperature in DMSO.

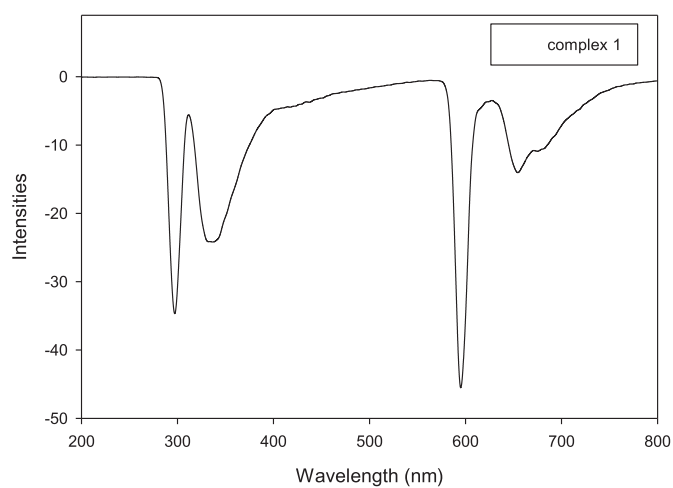


Fig. 6. Fluorescence spectrum of complex **1** with $\text{ex} = 598 \text{ nm}$ in DMSO at room temperature.

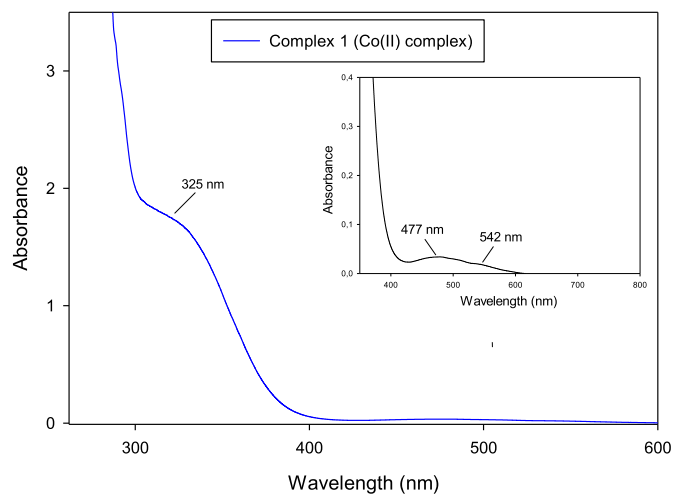


Fig. 8. Electronic spectra of complex **1** with inset showing DMSO- d_6 transition of the complex.

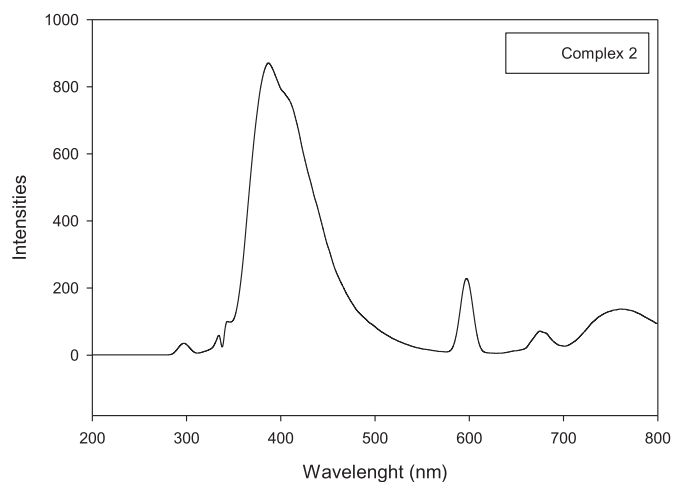


Fig. 7. Fluorescence spectrum of complex **2** with $\text{ex} = 338 \text{ nm}$ in DMSO at room temperature.

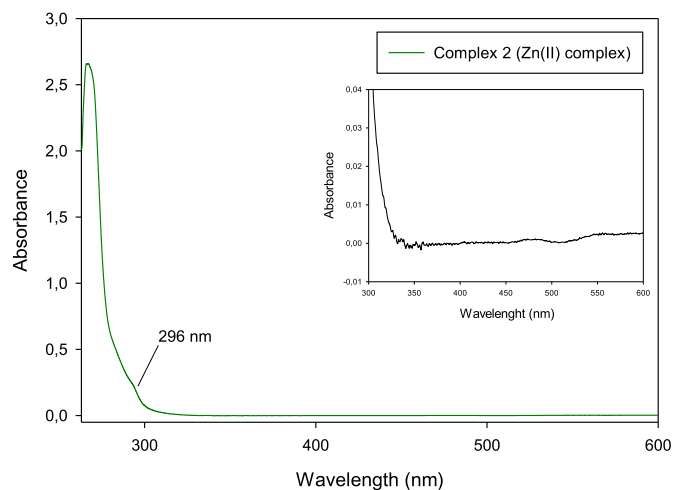


Fig. 9. Electronic spectra of complex **2** with inset showing no DMSO- d_6 transition for the complex.

emission was observed as crystalline compound **2** is formed from the amorphous solid ligands (picolinic acid and trimesic acid). Compound **1** exhibit no luminescent property which has been attributed to Co(II) ion acting as a quenching agent. The luminescent emission of **2** indicates that this complex may have potential application as sensors for optical and blue – light emitting materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.molstruc.2017.12.086>.

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