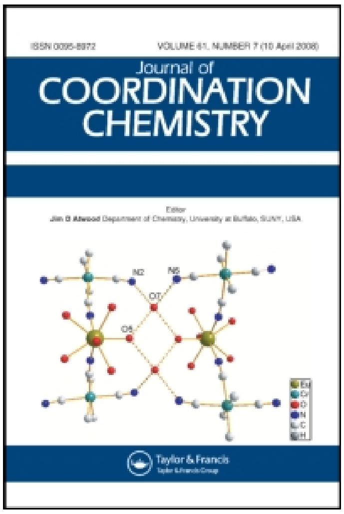

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Syntheses, characterizations and crystal structures of two new complexes, $[Co_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2(H_2O)_2]$ and $[Pb_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2]$

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Two new complexes, $[Co_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2(H_2O)_2]$ (**1**) and $[Pb_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2]$ (phen = 1,10-phenanthroline) (**2**), have been synthesized and structurally characterized by single crystal X-ray diffraction methods. There are two cocrystallized conformers of $[Co(CH_2{=}C(CH_3)CO_2)_2(phen)(H_2O)]$ in the asymmetric unit of **1** with the Co atoms displaying similar coordination modes. In the asymmetric unit of **2**, there exist two crystallographically independent $[Pb(CH_2{=}C(CH_3)CO_2)_2(phen)]$ molecules with the Pb atoms showing completely different coordination geometries. Weak intermolecular interactions such as hydrogen bonding and π–π stacking are responsible for the supramolecular assembly and stabilization of the crystal structures of **1** and **2**. The complexes are characterized by elemental analysis, IR spectra, and UV–Vis spectra. The fluorescent properties of **2** are also discussed.

Keywords: Cobalt(II); Lead(II); Mixed-ligand complexes; Crystal structures

1. Introduction

Rational design of solid crystalline materials with specific properties for a variety of physical and chemical applications is important for crystal engineering and materials science [1–3]. Non-covalent interactions, such as π–π stacking and hydrogen bonding, can generate structures defined as ‘‘supramolecular synthons’’ which can be crucial to the topochemical reactivity of molecules in the crystalline state [4, 5]. Aromatic π–π stacking interactions and hydrogen-bonding interactions are responsible for a wide array of phenomena in chemistry and biology, including organic transformations [3], organization of molecular solids [6], and molecular recognition [7]. 1,10-phenanthroline (phen) and other bidentate chelating ligands have been widely used as substitutes for amino acid side groups in biomimetic chemistry. Methacrylic acid, an O-donor anionic ligand, has been used in the synthesis of several metal carboxylate complexes [8–12]. However, there are few reported structures of mixed-ligand heavy metal complexes of methacrylate and N-heterocycles such as 1,10-phenanthroline, 2,2-bipyridine and

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4,4-bipyridine [13–16]. In this contribution, we present two mixed-ligand complexes, $[Co_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2(H_2O)_2]$ (**1**) and $[Pb_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2]$ (**2**) ($CH_2{=}C(CH_3)CO_2$ = methacrylate).

2. Experimental

All chemicals (reagent grade) were commercially available and used without further purification. Elemental analysis was performed using a Perkin–Elmer 2400 CHNS/O analyzer. The infrared spectrum in KBr pellets (4000–400 cm^{-1}) was recorded using a Perkin–Elmer FTIR-2000 spectrophotometer. UV–Vis spectra were recorded on a Perkin–Elmer Lambda-35 spectrophotometer in water. All the excitation and emission spectra were measured with an Aminco Bowman Series 2 with a xenon arc lamp as the excitation light source for the solid-state samples.

2.1. *Preparation of $[Co_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2(H_2O)_2]$ (1)*

Freshly prepared $Co(OH)_2$ (0.093 g, 1.0 mmol), obtained from 2.0 mL (1.0 M) NaOH to a stirred aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol) in 5 mL H_2O, was added to a stirred aqueous solution of 1,10-phenanthroline (0.198 g, 1.0 mmol) and methacrylic acid (0.076 g, 2.0 mmol) in 20 ml H_2O/methanol (v/v 1 : 1). The mixture was stirred for another 2 h and filtered, and the resultant filtrate was allowed to evaporate at room temperature. Red crystals were obtained 30 days later in a yield of 68% based on initial $Co(OH)_2$. Anal. Calcd for $C_{40}H_{40}Co_2N_4O_{10}$ (%): C, 56.24; H, 4.66; N, 6.58. Found: C, 56.21; H, 4.72; N, 6.56.

2.2. *Preparation of $[Pb_2(CH_2{=}C(CH_3)CO_2)_4(phen)_2]$ (2)*

The procedure of preparation of **2** is similar to that of **1**. Freshly prepared $Pb(OH)_2$ (0.241 g, 1.0 mmol), obtained from 2.0 mL (1.0 M) NaOH to a stirred aqueous solution of $Pb(NO_3)_2$ (0.331 g, 1.0 mmol) in 5 mL H_2O, was added to a stirred aqueous solution of 1,10-phenanthroline (0.198 g, 1.0 mmol) and methacrylic acid (0.076 g, 2.0 mmol) in 20 mL H_2O/methanol (v/v 1 : 1). The mixture was stirred for another 2 h, filtered, and the resultant filtrate was allowed to evaporate at room temperature. Colorless crystals were obtained 20 days later in a yield of 76% based on the initial $Pb(OH)_2$. Anal. Calcd for $C_{40}H_{36}N_4O_8Pb_2$ (%): C, 43.11; H, 3.21; N, 5.06. Found: C, 43.08; H, 3.25; N, 5.02.

2.3. *X-ray crystallography*

The reflection intensities of **1** and **2** were collected at 298 K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), by the $\Psi/2\vartheta$ scan method. Absorption corrections were applied using SADABS [17]. The structures were solved using SHELXL-97 [18] by direct methods, and all non-hydrogen atoms were refined with anisotropic displacement

Table 1. Summary of crystal data, data collection, structure solution and refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{40}H_{40}Co_2N_4O_{10}$	$C_{40}H_{36}N_4O_8Pb_2$
Formula weight	854.62	1115.111
432	Red block	Colorless block
Crystal size (mm^3)	$0.356 \times 0.288 \times 0.229$	$0.650 \times 0.380 \times 0.210$
Temperature	273(2)	273(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.1897(15)	9.2169(2)
b	13.1879(19)	11.5870(3)
c	16.562(2)	19.1033(5)
α	72.45(0)	102.5160(10)
β	76.45(0)	97.8670(10)
γ	73.15(0)	97.7150(10)
Volume (Å^3), Z	2004.42(174), 2	1944.39(8), 2
D_{Calcd} ($g\,cm^{-3}$), $F(000)$	1.416, 884	1.905, 1064
Absorpt. coeff. (mm^{-1})	0.889	8.704
Transmission range	0.746–0.829	0.761–0.872
θ Range (°)	0.962–28.49	0.992–28.41
Reflections collected	18828	38090
Unique reflections (R_{int})	9778 (0.0285)	9702 (0.0334)
Data	6411	7623
Parameters/restraints	519/0	488/0
Goodness-of-fit on F^2	0.991	1.021
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0522, 0.1347	0.0250, 0.0540
R_1, wR_2 (all data)	0.0845, 0.1572	0.0385, 0.0582
$\delta\rho_{\max}$, $\delta\rho_{\min}$ (e Å^{-3})	1.455, −0.384	1.279, −0.682

parameters by full-matrix least-squares methods on F^2. The hydrogen atoms associated with carbon atoms were generated geometrically, and the H_2O hydrogen atoms were located from the difference Fourier syntheses. Detailed information about the crystal data and structure determination are summarized in table 1. Selected interatomic distances and bond angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure descriptions*

3.1.1. Structure description of 1. Complex **1** consists of two crystallographically different, but chemically equivalent $[Co(CH_2{=}C(CH_3)CO_2)_2(phen)(H_2O)]$ molecules. Each cobalt atom is six-coordinate by two nitrogens of 1,10-phenanthroline and four oxygens, one from water and three from two different methacrylate groups, as shown in figure 1. One methacrylate is bidentate and the other is monodentate. The CoN_2O_4 chromophores display distorted octahedral geometries with the axial apical positions occupied by one methacrylate oxygen (O2 for Co1 and O7 for Co2) and one nitrogen of 1,10-phenanthroline (N2 for Co1 and N3 for Co2). The bond values of the CoN_2O_4 chromophores are normal (table 2) and compare to those of the related complexes [19].

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound **1**					
Co1–O2	2.034(2)	Co2–O7	2.035(2)	C1–C3	1.355(6)
Co1–O3	2.216(2)	Co2–O8	2.191(2)	C5–C7	1.388(5)
Co1–O4	2.157(2)	Co2–O9	2.1790(19)	C22–C23	1.367(5)
Co1–O5	2.088(2)	Co2–O10	2.093(2)	C25–C27	1.371(5)
Co1–N1	2.105(2)	Co2–N3	2.136(2)		
Co1–N2	2.139(2)	Co2–N4	2.104(2)		
O2–Co1–O5	91.34(10)	O2–Co1–O3	90.97(9)	N4–Co2–N3	77.80(9)
O2–Co1–N1	92.88(9)	O5–Co1–O3	94.61(8)	O7–Co2–O9	93.73(8)
O5–Co1–N1	104.83(9)	N1–Co1–O3	160.07(9)	O10–Co2–O9	93.33(8)
O2–Co1–N2	169.76(9)	N2–Co1–O3	99.23(9)	N4–Co2–O9	158.23(8)
O5–Co1–N2	86.98(9)	O4–Co1–O3	59.94(8)	N3–Co2–O9	98.22(8)
N1–Co1–N2	77.82(9)	O7–Co2–O10	91.21(9)	O7–Co2–O8	90.01(8)
O2–Co1–O4	90.34(9)	O7–Co2–N4	91.50(9)	O10–Co2–O8	153.23(8)
O5–Co1–O4	154.53(9)	O10–Co2–N4	107.69(9)	N4–Co2–O8	99.00(8)
N1–Co1–O4	100.47(8)	O7–Co2–N3	168.00(9)	N3–Co2–O8	96.94(8)
N2–Co1–O4	95.52(9)	O10–Co2–N3	86.97(9)	O9–Co2–O8	59.92(7)
Compound **2**					
Pb1–O1	2.336(2)	Pb1–N1	2.673(3)	Pb2–O8	2.287(2)
Pb1–O3	2.419(3)	Pb1–O4	2.752(3)	Pb2–N4	2.649(3)
Pb1–N2	2.599(3)	Pb1–O4#1	3.073(3)	Pb2–O7	2.681(2)
Pb1–O2	2.629(3)	Pb2–O5	2.391(2)	Pb2–O6	2.738(3)
Pb2–N3	2.574(3)				
O1–Pb1–O3	83.17(10)	N2–Pb1–O4	126.51(9)	O8–Pb2–N4	75.69(9)
O1–Pb1–N2	84.22(9)	O2–Pb1–O4	85.17(8)	O5–Pb2–N4	136.42(9)
O3–Pb1–N2	76.84(9)	N1–Pb1–O4	159.65(9)	N3–Pb2–N4	63.23(9)
O1–Pb1–O2	52.12(8)	O1–Pb1–O4#1	140.47(8)	O8–Pb2–O7	51.85(8)
O3–Pb1–O2	119.48(9)	O3–Pb1–O4#1	118.64(9)	O5–Pb2–O7	119.80(8)
N2–Pb1–O2	126.35(8)	N2–Pb1–O4#1	130.57(8)	N3–Pb2–O7	126.48(8)
O1–Pb1–N1	75.60(9)	O2–Pb1–O4#1	88.66(8)	N4–Pb2–O7	76.03(8)
O3–Pb1–N1	135.48(9)	N1–Pb1–O4#1	102.09(8)	O8–Pb2–O6	84.70(9)
N2–Pb1–N1	62.60(9)	O4–Pb1–O4#1	84.87(8)	O5–Pb2–O6	50.13(8)
O2–Pb1–N1	76.01(8)	O8–Pb2–O5	84.18(9)	N3–Pb2–O6	126.52(8)
O1–Pb1–O4	86.83(9)	O8–Pb2–N3	84.19(9)	N4–Pb2–O6	157.36(9)
O3–Pb1–O4	49.73(8)	O5–Pb2–N3	76.75(9)	O7–Pb2–O6	83.02(8)

Symmetry transformations used to generate equivalent atoms: $\#1 = -x+2, -y+2, -z+1$.

The crystallographically different $[\mathrm{Co(CH_2{=}C(CH_3)CO_2)_2(phen)(H_2O)}]$ molecules are linked by strong π–π stacking interactions with the neighboring 1,10-phenanthroline distances of 3.494 Å and strong hydrogen bonding interactions (between oxygen of water and oxygen of methacrylates) into dimers, which are assembled into 2D layers parallel to (100) by C–H ⋯ O weak hydrogen bonds, where the 1,10-phenanthroline groups donate hydrogen atoms to the neighboring carboxylate and water oxygens (figure 2) [20].

3.1.2. Structure description of 2. Compound **2** consists of two crystallographically independent $[\mathrm{Pb(CH_2{=}C(CH_3)CO_2)_2(phen)}]$ molecules. Pb1 is surrounded by two nitrogen atoms (N1, N2) and five oxygen atoms, of which four come from two chelating carboxylate groups and one comes from a bidentate bridging carboxylate oxygen. The seven-coordinate Pb1 atoms are linked by bidentate chelating plus monodentate bridging carboxylate groups into a four-membered $\mathrm{Pb_2O_2}$ rhombic ring with Pb–Pb separation of 4.305 Å, as shown in figure 3. Pb1–N bond distances (2.599(3), 2.673(3) Å) and Pb1–O bond distances (ranging from 2.336(2) to 3.073(3) Å) are comparable to those of related complexes [21, 22]. The seven-coordinate Pb1 is a distorted pentagonal

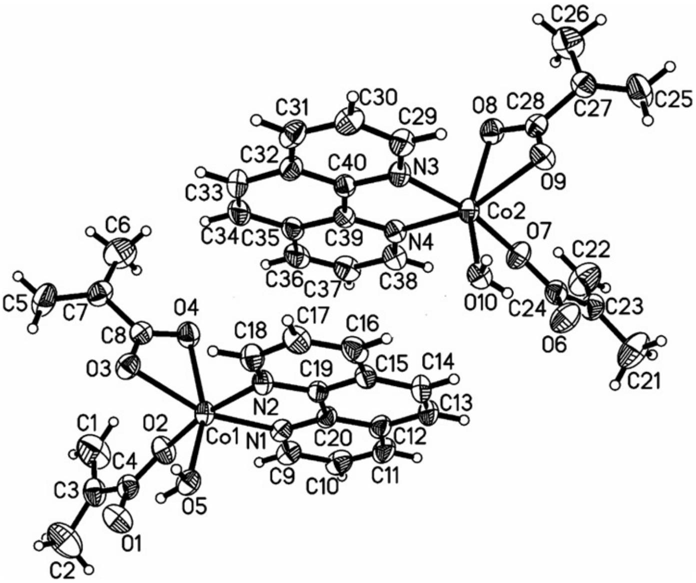

Figure 1. Coordination environment of Co along with the atomic labeling of **1** (displacement ellipsoids are drawn at 30% probability).

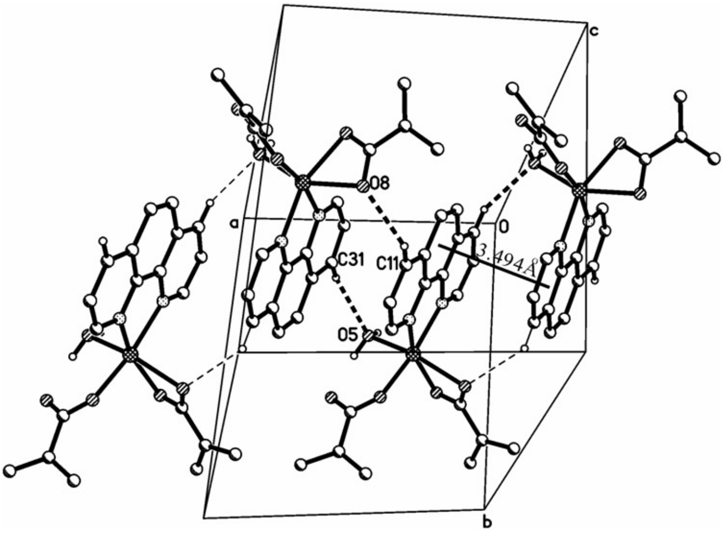

Figure 2. Partial packing of **1** showing the formation of chains along [100] built from hydrogen bonds (dashed lines) and π–π stacking interaction. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

bipyramid, with the apical positions occupied by O1 and O4$^{\#1}$; the polyhedron is significantly distorted due to long Pb1-O4$^{\#1}$ distances, perhaps from the lone pair electrons.

Pb2, surrounded by two nitrogen atoms (N3, N4) and four oxygen atoms, which come from two chelating carboxylate groups, exhibits a distorted pentagonal pyramid

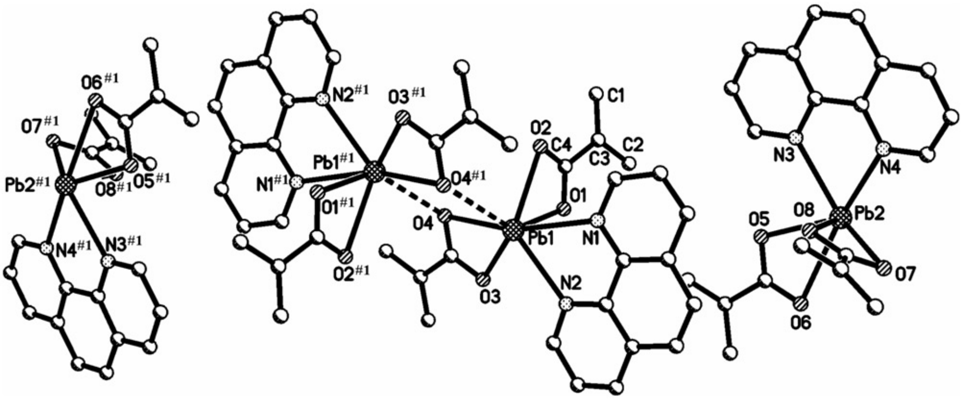

Figure 3. Coordination environment of Pb along with the atomic labeling of 2 (displacement ellipsoids are drawn at 30% probability; symmetry transformations used to generate equivalent atoms: $\#1 = -x + 2, -y + 2, -z + 1$).

geometry with the apical positions occupied by carboxylate O8. The Pb2-N3 distance (2.574(3) Å) is shorter than the Pb2–N4 distance (2.649(3) Å), similar to $[Pb(tbz)_2\,\mu\text{-}NO_3)_2]$ [21]. The *cis* bond angles at Pb2 from the apical O8 atom range from 51.85(8)° to 84.70(9)°, suggesting a significant deviation from a perfect pentagonal pyramid. All coordinated atoms reside in one hemisphere and Pb2 is shifted by 0.662(2) Å from the basal plane, the likely location of the "lead(II) lone pair" [23].

The crystallographically different $[Pb(CH_2{=}C(CH_3)CO_2)_2(phen)]$ molecules are linked by weak Pb–O interactions (Pb1–O4 = 3.073 Å, Pb2–O7 = 3.572 Å) into dimers, which are assembled by π–π stacking with neighboring 1,10-phenanthroline distance of 3.637 Å and C–H $\cdots$ O weak hydrogen bonding into 2D networks parallel to (011) from 1,10-phenanthroline groups donate hydrogen atoms to neighboring carboxylate oxygen atoms (figure 4) [20].

3.2. *Infrared spectra*

The infrared spectrum of **1** shows bands at 3069 and 2954 cm^{-1} attributed to the unsaturated $\nu_{=C\text{–}H}$ and the $\nu_{C\text{–}H}$ stretching vibrations, respectively. The absorption of 1645 cm^{-1} is from methacrylate $\nu_{C=O}$ stretching. Strong absorption bands at 1557, 1514, 1453 and 1425 cm^{-1} may be attributed to phenyl group C–C stretches.

The infrared spectrum of **2** shows similar bands at 3069 and 2954 cm^{-1}, $\nu_{=C\text{–}H}$ stretching vibrations, 1631 cm^{-1} $\nu_{C=O}$ stretching and 1615, 1597, 1542, 1451 cm^{-1}, attributed to C–C stretching vibrations of the *phen* group [24].

3.3. *UV–Vis spectra*

Compounds **1** and **2** possess similar absorption bands at 283–241, 237–211, and 207–190 nm, which should be assigned to B, E2 and E1 bands of 1,10-phenanthroline in aqueous solution. Comparing to the free ligand, the absorptions are slightly blue-shifted. The weak absorption at 301–285 nm could be assigned to the $n \rightarrow \pi^*$ transition of methacrylate.

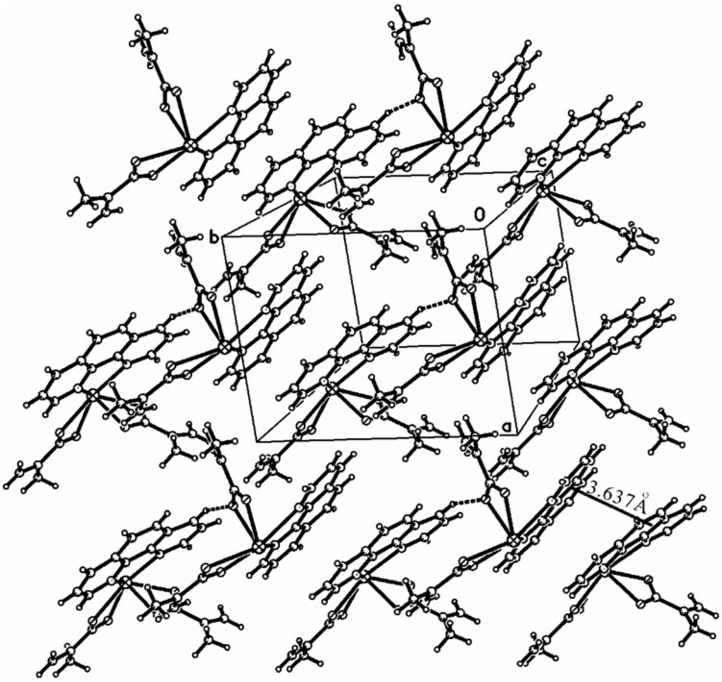

Figure 4. The 2D structure of **2** built from π–π stacking interactions.

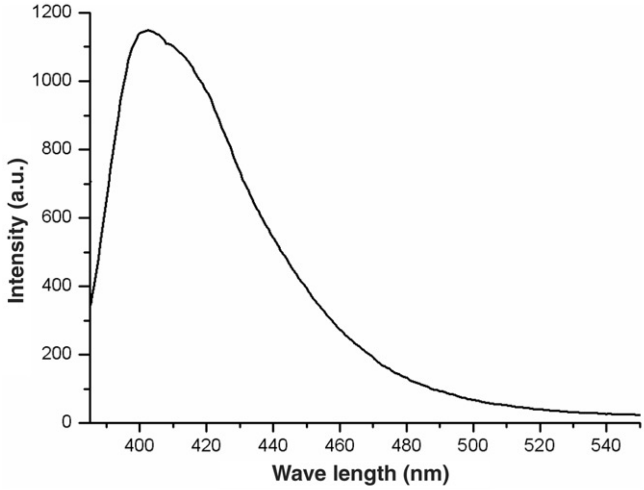

Figure 5. Fluorescent emission spectrum of solid **2** at room temperature.

3.4. *Fluorescence spectra*

The solid-state fluorescence spectra of **2** at room temperature are depicted in figure 5. **2** exhibits stronger fluorescence than the free ligand with maximum emission at ca 402 nm upon excitation at 373 nm, assigned to the ligand–ligand charge transfer $\pi_L \rightarrow \pi_L{}^*$ transition from 1,10-phenanthroline [25]. Free 1,10-phenanthroline displays weak luminescence at ca 365 nm in the solid state at room temperature. Fluorescence enhancement of **2** may be due to coordination and crystal packing interactions in the solid state. The significant red-shift of the luminescence may be due to the inter-planar *phen-phen* π–π stacking interactions, which results in a decrease in the HOMO-LUMO energy gap [26].

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