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Zinc(II) and cadmium(II) complexes based on 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-(4-methoxyphenyl)pyrimidine-4-carboxylic acid: Synthesis, structure and luminescence

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ABSTRACT

Zinc(II) and cadmium(II) complexes, $ZnL_2 \cdot 0.5H_2O$, $ZnL_2 \cdot 2MeOH$ and $CdL_2 \cdot 1.5H_2O$, based on a new hybrid compound, 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-(4-methoxyphenyl)pyrimidine-4-carboxylic acid (HL), have been synthesized. They are the first examples of metal complexes with pyrazolylpyrimidinecarboxylates. The complex $ZnL_2 \cdot 2MeOH$ was structurally characterized. It has mononuclear structure; zinc atom is in the distorted octahedral coordination polyhedron 4N + 2O formed by donor atoms of two coordinated L^- ions. The compounds HL, $ZnL_2 \cdot 0.5H_2O$ and $CdL_2 \cdot 1.5H_2O$ manifest bright blue photoluminescence.

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Among various pyrazolylpyrimidines, 2-(pyrazolyl)pyrimidines have attracted most attention as the ligands for the synthesis of transition metal complexes [1–19]. These complexes are of fundamental and practical importance since they manifest various kinds of biological and catalytic activity [8,14,19]. Other pyrimidine-based compounds, pyrimidine-4(6)-carboxylic acids and corresponding carboxylates also were reported as the ligands [20–23]. In this context, studying pyrazolylpyrimidines and their complexes with metals, we decided to combine the pyrazolyl and the carboxylic groups within a single molecule on the base of the pyrimidine core and to study coordination behavior of a new hybrid compound, 2-(3,5-dimethyl-1H-pyrazol-1-yl)-6-(4-methoxyphenyl)pyrimidine-4-carboxylic acid (HL, Scheme 1), with respect to zinc(II) and cadmium(II). It ought to note, that previously some of us synthesized a series of 2-hydrazinylpyrimidine-4(6)carboxylic acids and used them for the preparation of reagent indicator paper for the detection of iron(II) and iron(III) [24]. In the present work we modified one of these compounds to obtain HL. To the best of our knowledge, the complexes reported here are the first examples of compounds based on pyrazolylpyrimidinecarboxylic acids. Taking into account that the complexes of zinc(II) and cadmium(II) with heteroaromatic ligands are one of the main groups of luminescent compounds [25–28], we were also endeavored to obtain compounds demonstrating luminescence. In this communication we report the synthesis and study of four new compounds, *i.e.*, HL, $ZnL_2 \cdot 0.5H_2O(1)$, $ZnL_2 \cdot 2MeOH(2)$ and $CdL_2 \cdot 1.5H_2O(3)$.

A new hybrid heteroaromatic compound, HL (Scheme 1), can be obtained by condensation of 2-hydrazinyl-6-(4-methoxyphenyl) pyrimidine-4-carboxylic acid (4) with acetylacetone [29]. The compound 4 and its phenyl analog previously were used for preparation of reagent paper by treating a modified chromatographic paper based on aldehyde cellulose [24]. The complexes 1 and 3 can be prepared as powder products by the reaction of corresponding acetate salt with HL in MeOH solutions at M:HL = 1:2 molar ratio (Scheme 1) [30,31]. IR-spectra of these compounds are similar [30,31]. The positions of the stretching-deformation vibrations of heteroaromatic rings, $(\nu + \delta)_{\text{ring}}$, in IR-spectra of these complexes are changed in comparison with the spectrum of HL. The bands of carboxylic group in the spectra of 1 and 3 also shifted. The far-IR spectra of the complexes exhibit the bands of $\nu(M-L)$ vibrations. These observations are consistent with the coordination of the heteroaromatic rings and carboxylic group of L⁻ ions. Water molecules seem to be noncoordinated. Attempts to crystallize 1 from MeOH solution afforded single crystals of 2 [32].

According to X-ray diffraction data [33], the structure of 2 is molecular mononuclear (Fig. 1). Two L^- ions (carboxylic group is deprotonated) are coordinated to zinc atom through N(1), N(3) and O(1) atoms adopting

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Scheme 1. The synthesis of HL and complexes 1-3.

thus tridentate chelating coordination mode. The coordination geometry around zinc atom is distorted octahedral (4 N + 20). As a result of the ligand coordination, practically planar ZnCN₃ and ZnC₂NO chelate cycles are closed. The (hetero)aromatic system of L⁻ ligand is nearly planar. The pyrazolyl and methoxyphenyl groups are rotated by 5.4° and 10.0° in respect to the pyrimidine plane. The structure is stabilized through formation of hydrogen bonds (O(1)···H(53)' 2.431 Å, O(2)···H(56)' 2.516 Å, O(1 S)···H(55)' 2.518 Å) (Fig. 2). MeOH molecules form hydrogen bonds with non-coordinated O atoms of carboxylic group (O(1)···H(1 S) 1.891 Å).

Single crystals of 2 become non-transparent within *ca.* several days probably due to loss of MeOH molecules. IR-spectra of 1 and decomposition product of single crystals of 2 are almost identical which induces to think that structures for 1 and probably for 3 are similar.

The compounds HL, 1 and 3 manifest bright photoluminescence in the solid state, the excitation and emission spectra are displayed in Figs. 3–5. The spectra of the compounds display a broad emission band with two maxima (for HL and 3) or an unsymmetrical band with a shoulder (for 1). The origin of luminescence of HL, having an extended conjugated π -system, seems to be due to $\pi^* \rightarrow \pi$ transitions. Since the profile and location of the emission bands in the spectra of the complexes are similar to those in the spectrum of HL, it seems to be reasonable that the luminescence mechanism for the complexes can be attributed to intra-ligand transitions as usual for zinc(II) and



Fig. 1. The molecule $[ZnL_2]$ in the structure of 2. Selected bond lengths (Å) and bond angles (°): Zn(1)-N(1), 2.185(1); Zn(1)-N(3), 2.040(1); Zn(1)-O(1), 2.162(1); N(3)-Zn(1)-N(3)#1, 163.88 (7); N(3)-Zn(1)-O(1), 75.66(4); N(3)=1-Zn(1)-O(1), 92.87(4); N(3)-Zn(1)-O(1)#1, 92.87(4); N(3)=1-Zn(1)-O(1)#1, 75.66(4); O(1)-Zn(1)-O(1)#1, 90.36(6); N(3)-Zn(1)-N(1), 74.36(5); N(3)=1-Zn(1)-N(1), 116.90(5); O(1)-Zn(1)-N(1), 149.95(4); O(1)=1-Zn(1)-N(1), 93.04(5); N(3)=2n(1)-N(1)=1, 16.90(5); N(3)=1-Zn(1)-N(1)=1, 149.95(4); O(1)=1-Zn(1)-N(1)=1, 149.95(4); O(1)=1-Zn(1)-N(1)=



Fig. 2. Packing of the molecules in the structure of 2.



Fig. 3. Excitation (solid line, λ_{em} =420 nm) and emission (dashed line) spectra of HL, λ_{exc} =350 nm. Spectra were recorded on Cary Eclipse spectrophotometer, ex. slit 5 nm, em. slit 5 nm, PMT voltage 500 V.



Fig. 4. Excitation (solid line, λ_{em} =430 nm) and emission (dashed lines) spectra of 1, a) λ_{exc} =350 nm, b) λ_{exc} =380 nm, c) λ_{exc} =390 nm. Spectra were recorded on Cary Eclipse spectrophotometer, ex. slit 5 nm, em. slit 5 nm, PMT voltage 500 V.



Fig. 5. Excitation (solid line, $\lambda_{em} = 430 \text{ nm}$) and emission (dashed lines) spectra of 3, a) $\lambda_{exc} = 350 \text{ nm}$, b) $\lambda_{exc} = 380 \text{ nm}$. Spectra were recorded on Cary Eclipse spectrophotometer, ex. slit 5 nm, em. slit 5 nm, PMT voltage 500 V.

In summary, a series of zinc(II) and cadmium(II) complexes, ZnL₂ \cdot 0.5H₂O, ZnL₂ \cdot 2MeOH and CdL₂ \cdot 1.5H₂O (HL = 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-(4-metoxyphenyl)pyrimidine-4-carboxylic acid) have been synthesized. The compounds HL, ZnL₂ \cdot 0.5H₂O and CdL₂ \cdot 1.5H₂O manifest bright blue photoluminescence.

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Appendix A. Supplementary Material

CCDC 804373 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac. uc/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.02.027.

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- [29] Synthesis of HL. A mixture of 2-hydrazinyl-6-(4-methoxyphenyl)pyrimidine-4carboxylic acid (3.85 mmol, 1.0 g) and acetylacetone (4.85 mmol, 0.5 ml) in 30 ml of EtOH was refluxed for 5 h. After cooling, the foam precipitate obtained was filtered off and washed with EtOH. The precipitate was recrystallized from EtOH and dried *in vacuo*. Yield: 1 g (80%). Anal. calcd. for C₁₇H₁₆N₄O₃: C, 63.0; H, 5.0; N, 17.3. Found: C, 62.5; H, 4.9; N, 17.0%. M.p. 197–199 °C. ¹H NMR (CDCl₃, 6, ppm): 2.30 (s, 3H, Me), 2.81 (s, 3H, Me), 3.88 (s, 3H, MeO), 6.08 (s, 1H, 4 – H_{pyrazole}), 7.02 (d, *J* = 8.8 Hz, 2H, Ph), 8.12 (d, *J* = 8.8 Hz, 2H, Ph), 8.25 (s, 1H, 5 – H_{pyrimidine}). Selected IR data: 3150, 1736, 1702, 1592 ($(\nu + \delta)_{ring}$), 1541 ($(\nu + \delta)_{ring}$), 1423, 1258, 1174, 1027, 990, 881, 839, 772, 745, 586, 528, 511, 495 cm⁻¹. A high-resolution mass spectrum (direct introduction of a sample to the ionic source): Anal. calcd. for C₁₇H₁₆N₄O₃: *M* = 324.1217. Found: *m*/z 324.1219 [M⁺].
- [30] Synthesis of 1. A suspension of HL (0.150 mmol, 48.7 mg) in 2 ml of warm MeOH (*ca.* 40 °C) was added to a solution of Zn(OAc)₂ 2H₂O (0.075 mmol, 16.5 mg) in 1 ml of warm MeOH (*ca.* 40 °C). Beige precipitate was formed immediately. Reaction mixture was refluxed for 1 h and then allowed to stay at room temperature overnight. The powder product was separated from the mother liquor by filtration and washed according to the following technique. MeOH (2 ml) was added to precipitate; the mixture was heated for 3 h and allowed to stay for 2 days at room temperature. After that, the precipitate was filtered off and dried in ambient air. Yield: 40.0 mg (74%). Anal. calcd. for C₃₄H₃₁N₈O_{6.5}Zn: C, 56.6; H, 4.3; N, 15.6. Found: C, 56.5; H, 4.3; N, 15.5%. Selected IR data: 3414 (H₂O), 1656 (CO), 1596 (($\nu + \partial$ _{ring}), 1541 (($\nu + \partial$ _{ring}), 1421, 1257, 1178, 1013, 978, 887, 846, 778, 744, 597, 537, 509, 442 (Zn–O), 244 (Zn–N), 178, 164 cm⁻¹.
- [31] Synthesis of 3. A suspension of HL (0.150 mmol, 48.7 mg) in 2 ml of warm MeOH (*ca.* 40 °C) was added to a solution of Cd(OAC)₂ · 2H₂O (0.075 mmol, 20.0 mg) in 1 ml of warm MeOH (*ca.* 40 °C). Light beige precipitate was formed immediately. Reaction mixture was refluxed for 2 h and then allowed to stay at room temperature for 3 days. The precipitate was filtered off, washed with MeOH and dried in ambient air. Yield: 48.0 mg (81%). Anal. calcd. for $C_{34}H_{33}$ CdN₈O_{7,5}: C, 52.0; H, 4.2; N, 14.3. Found: C, 51.9; H, 4.1; N, 14.1%. Selected IR data: 3391 (H₂O), 1650 (CO), 1590 (($\nu + \delta$)_{ring}), 1537 (($\nu + \delta$)_{ring}), 1417, 1265, 1188, 1006, 981, 888, 846, 776, 742, 593, 524, 507, 434 (Cd–O), 223 (Cd–N), 180, 168 cm⁻¹.
- [32] A small tip of a spatula of ZnL₂ · 0.5H₂O was dissolved in MeOH (2 ml). Beige single crystals were obtained in a month. They were used in X-ray diffraction analysis and their composition was determined as ZnL₂ · 2MeOH.
- [33] Single crystal data for 2 were collected at 150 K with MoK_{α} radiation (λ =0.71073 Å) using a Bruker Nonius X8Apex CCD diffractometer equipped with graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation. Crystallographic data for 2: C₃₆H₃₆N₈O₈Zn, *M*=774.10, 0.15×0.12×0.08 mm³, monoclinic, *C2*/c, *a*=23.0795(6), *b*=10.1204(2), *c*=21.6279(5) Å, *β*=134.578 (2)°, *V*=3598.3(1) Å³, *Z*=4, *D_c*=1.429 g/cm³, Goodness-of-fit on *F*²=1.062, *R*₁=0.0275, *wR*₂=0.0792 [*I*>2 o(1)], *R*₁=0.0310, *wR*₂=0.0812.