



# Coordination capabilities of metal ions and steric features of organic ligands affecting formation of mono- or binuclear zinc(II) and cadmium (II) pivalates

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## ABSTRACT

Reactions between zinc(II) or cadmium(II) pivalates and 2,2'-bipyridine, various substituted 1,10-phenanthroline derivatives or 2,2':6',2''-terpyridine have resulted in ten mono- and binuclear complexes with general formula  $[M(\text{piv})_2L]$  or  $[\text{Cd}_2(\text{piv})_4L_2]$ , where piv is the pivalate anion, L is N,N'- or N,N',N''-donor ligand, and M = Zn(II), Cd(II). Molecular and crystal structures as well as optical properties of the obtained homometallic complexes are reported and discussed. Preferable formation of binuclear cadmium compounds depending on type of the ligand are studied and clearly explained by means of DFT calculations.

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## 1. Introduction

It is known that a great number of coordination compounds of  $d^{10}$  metals with aromatic ligands possess interesting photophysical properties allowing one to use these objects in various fields of materials science as photosensitizers and OLED or LED components [1]. The luminescent properties of these compounds depend on the nature of ligands used [2], crystal packing, and presence of solvate molecules [3]. The crystals of these compounds contain molecules of complexes packed in isolation or interacting with each other through intermolecular interactions [4] (H-bonds, stacking [5], halogen–halogen interactions [6], etc.). This fact allows us to vary photophysical characteristics of crystals. The information about the structures of these complexes, role of structural effects, and features of ligand coordination (steric factors, intra- and intermolecular interactions) as well as possibilities for varying the luminescent properties of  $d^{10}$  metal complexes with aromatic ligands when changing the nature of metals in them (for example, blueshift or redshift because of ligand coordination) can be useful for the directed synthesis of photoactive  $d$ -4f heterometallic com-

plexes, in which  $d^{10}$  blocks are present that are capable of sensitizing luminescence of lanthanide ions [7]. In addition, it is important to study this type of complexes for modeling and studying the nature of the structure-forming factors determining the effectiveness of stacking interactions. This is required for the development of fundamental principles of the molecular design of dynamic molecular crystals with tunable photoluminescent [8], electrophysical [9], magnetic, and other practically useful characteristics [10].

From this point of view, carboxylate complexes are objects suitable for these studies, since the carboxylic acid anions have a wide range of possibilities to bind the metal ion, including examples in which metal centers can be subsequently coordinated by other N- or O-donor ligands. At the same time, the carboxylate group in some cases is capable of acting as a bridging ligand, binding from two to four atoms simultaneously. At the same time, as for photoactivity of the compounds, carboxylate ligands (especially those containing aromatic substituents) can be considered as promising antennas for enhancing luminescence of lanthanide ions in  $d$ -4f complexes [7f,8b,11].

In this paper, ten new molecular Zn(II) and Cd(II) complexes with pivalate anions and N-donor heterocyclic ligands were synthesized and characterized by X-ray diffraction as well as IR, UV–Vis, NMR, and luminescence spectroscopies. Pivalate anions were

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selected because of good solubility of the corresponding metal complexes in organic solvents; in addition, the role of the optically inactive *tert*-butyl substituent was taken into account, which makes it possible to determine the spectral characteristics of the aromatic ligands, which are parts of the complexes.

## 2. Material and methods

New compounds were synthesized in acetonitrile (>99%) media in air. 2,2'-Bipyridine (99%, Alfa Aesar), 4,7-diphenyl-1,10-phenanthroline (batho, 98+%, Alfa Aesar), 2,9-dimethyl-1,10-phenanthroline (neocup, 99+%, Ruka AG), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocup, 98%, Acros Organics), and 2,2':6',2''-terpyridine (terpy, 97%, ABCR) were used as the starting reagents. Starting pivalate complexes  $[Zn(piv)_2]_n$  and  $\{Cd(piv)_2\}$  were synthesized according to the previously reported procedures [12]. Elemental analysis of the resulting compounds was carried out on a Carlo Erba automatic C,H,N,S-analyzer.

### 2.1. X-ray diffraction

The X-ray diffraction data set for **1–10** was collected on a Bruker APEX II diffractometer equipped with a CCD camera and a graphite monochromated  $MoK\alpha$  radiation source ( $\lambda = 0.71073 \text{ \AA}$ ) [13]. Semiempirical absorption corrections were applied for all complexes except for the structure of complex **5** [14]. X-ray diffraction structures were solved and refined using SHELX-97 or refined using SHELXL-97 or SHELXL-2014 [15]. Positions of disordered Me-groups in *tert*-butyl fragment (at C(2) atom) of Piv in **1\*** were localized in difference Fourier maps and refined with occupancies of 0.763(4) and 0.237(4). Positions of disordered Me-groups in *tert*-butyl fragment (at C(2) atom) of Piv in **2** were localized in difference Fourier maps and refined with occupancies of 0.752(12) and 0.248(12). Crystallography parameters and structure refinement details are listed in Table S1. Powder X-ray diffraction data were collected using a Bruker D8 Advance diffractometer ( $CuK\alpha$ ,  $\lambda = 1.54 \text{ \AA}$ , Ni-filter, LYNXEYE detector, geometry reflection).

### 2.2. Spectral measurements

IR spectra of the compounds were recorded on a Perkin Elmer Spectrum 65 spectrophotometer equipped with a Quest ATR Accessory (Specac) by the attenuated total reflectance (ATR) in the range 400–4000  $cm^{-1}$ . UV–Vis reflectance spectra were recorded at room temperature using a Cary 5000 spectrometer (Agilent) in the 200–800 nm range. Luminescent spectra were measured with a Perkin Elmer LS-55 spectrofluorimeter.

$^1H$  and  $^{13}C$  NMR spectra were recorded from  $CDCl_3$  solutions of compounds with a Bruker Avance 600 spectrometer. The measurements were performed using the residual signals of  $CDCl_3$  ( $^1H$  7.26 ppm,  $^{13}C$  77.16 ppm) as a reference. Data acquisition and processing were performed with the Topspin 2.1 and Mestrenova 9.0.0 software, respectively.

### 2.3. Computational details

The density functional theory (DFT) calculations were performed using the Gaussian 09 program package [16] with the B3LYP/def2svp approximation. The stationary points on the potential energy surfaces were located by full geometry optimization and checked for the stabilities of the DFT wave function. Mechanism of dimerization of the zinc(II) complex has been studied by means of search for all stationary points on the reaction path. Localization of transition states has been performed with the use of standard technique of the Gaussian program (opt = (ts, calcfc)).

The belonging of the found transition states to the discussed mechanism was ascertained by means of gradient descent on the positive and negative directions of the transition vector, which has imaginary eigenvalue (imaginary frequency). Structural visualizations presented in Figs. 6 and 7 were prepared using the program suite ChemCraft [17] with the calculated atomic coordinates as the input parameters.

### 2.4. Synthesis of complexes 1–10

The corresponding ligand (1 mmol) was added to a MeCN solution (40 mL) of the corresponding metal pivalate (1 mmol). The resulting mixture was stirred at  $t = 60 \text{ }^\circ C$  for 2 h, filtered off, and slowly cooled to room temperature. The solution was kept at room temperature, and crystals precipitated for 6–48 h. In some cases, single crystals suitable for X-ray diffraction studies were obtained after recrystallisation from MeCN (slow evaporation under reduced pressure).

#### 2.4.1. $[Zn(piv)_2(bpy)]$ (**1**)

Colorless crystals. Yield: 77%. Calc. for  $C_{20}H_{26}N_2O_4Zn$  (%): C, 56.68%; H, 6.18%; N, 6.61%. Found (%): C, 56.49%; H, 6.40%; N, 6.56%. IR ( $cm^{-1}$ ): 3076(w), 2969(m), 2934(w), 2867(w), 1607(m), 1588(m), 1578(s), 1562(vs), 1475(s), 1445(s), 1404(s), 1360(s), 1318(m), 1289(w), 1251(w), 1220(s), 1181(w), 1164(w), 1124(w), 1109(w), 1056(w), 1040(w), 1024(m), 1011(w), 977(w), 939(w), 894(m), 809(m), 792(m), 773(vs), 737(s), 652(m), 632(m), 615(s), 540(w), 459(w), 422(s).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta = 8.97$  (s, 2H, bpy), 8.16 (d,  $J = 7.8$  Hz, 2H, bpy), 8.03 (t,  $J = 8.0$  Hz, 2H, bpy), 7.58 (s, 2H, bpy), 1.17 (s, 18H, Me).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta = 189.21, 149.92, 140.37, 126.49, 120.99, 38.47, 28.32$ .

#### 2.4.2. $[Cd_2(piv)_4(bpy)_2]$ (**2**)

Colorless crystals. Yield: 55%. Calc. for  $C_{40}H_{52}Cd_2N_4O_8$  (%): C, 51.02%; H, 5.57%; N, 5.95%. Found (%): C, 51.38%; H, 5.65%; N, 6.03%. IR ( $cm^{-1}$ ): 2955(wb), 1592(w), 1579(w), 1537(s), 1492(m), 1477(m), 1438(m), 1405(s), 1368(m), 1356(s), 1319(w), 1249(w), 1219(m), 1176(w), 1153(m), 1062(w), 1016(m), 894(m), 806(w), 792(w), 765(s), 736(m), 649(w), 625(w), 603(m), 528(w), 412(m).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta = 8.87$  (dd,  $J = 4.9, 1.6$  Hz, 4H, bpy), 8.16 (d,  $J = 8.1$  Hz, 4H, bpy), 8.01 (td,  $J = 7.8, 1.7$  Hz, 4H, bpy), 7.55 (dd,  $J = 7.5, 5.1$  Hz, 4H, bpy), 1.17 (s, 36H, Me).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta = 188.62, 150.59, 149.91, 139.97, 126.11, 121.66, 38.78, 28.61$ .

#### 2.4.3. $[Zn(piv)_2(neocup)]$ (**3**)

Pale yellow crystals. Yield: 71%. Calc. for  $C_{24}H_{30}N_2O_4Zn$  (%): C, 60.57%; H, 6.35%; N, 5.89%. Found (%): C, 60.96%; H, 6.07%; N, 6.24%. IR ( $cm^{-1}$ ): 2959(m), 2866(w), 1593(s), 1566(s), 1502(s), 1481(vs), 1456(m), 1399(vs), 1347(vs), 1298(w), 1217(vs), 1151(m), 1036(w), 1002(w), 941(w), 896(s), 867(vs), 845(m), 807(m), 790(m), 777(s), 733(s), 680(m), 658(m), 615(vs), 551(s), 462(w).  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta = 8.35$  (d,  $J = 8.3$  Hz, 2H,  $C_{Ar-H}$ ), 7.85 (s, 2H,  $C_{Ar-H}$ ), 7.71 (d,  $J = 8.3$  Hz, 2H,  $C_{Ar-H}$ ), 3.15 (s, 6H, Me(neocup)), 1.17 (s, 18H, Me(piv)).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta = 186.60, 161.02, 140.75, 139.05, 127.21, 126.56, 125.81, 38.96, 28.55, 25.00$ .

#### 2.4.4. $[Cd(piv)_2(neocup)]$ (**4**)

Yellow crystals. Yield: 86%. Calc. for  $C_{24}H_{30}CdN_2O_4$  (%): C, 55.13%; H, 5.78%; N, 5.36%. Found (%): C, 55.51%; H, 6.09%; N, 5.52%. IR ( $cm^{-1}$ ): 2974(m), 2934(w), 2866(w), 1613(w), 1591(w), 1531(vs), 1502(vs), 1482(vs), 1456(s), 1411(vs), 1372(s), 1356(vs), 1294(w), 1223(s), 1156(m), 1149(w), 1119(w), 1035(m), 989(w), 937(w), 898(vs), 867(s), 844(m), 809(s), 792(m), 772(m), 732(s), 680(m), 654(m), 608(vs), 551(m), 530(m), 484(w), 460(w),

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