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Intramolecular cyclization - decyclization of new sterically hindered diiminophenol. Synthesis and coordination abilities

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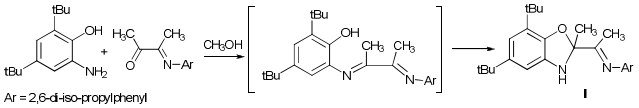
The new sterically hindered benzoxazole **I** was synthesized by the reaction of 3-(2,6-diisopropylphenylimino)butan-2-one and 2-amino-4,6-di-tert-butylphenol. It is shown that compound **I** is in equilibrium with the open enamine form in solution.
The coordination abilities of **I** have been studied. The ligand **I** is shown to demonstrate either a neutral coordination type in complex with cadmium iodide or monoanionic type in cadmium complexes obtained by the interaction of **I** with Me_2Cd.

Introduction

Schiff base ligands have been extensively studied mainly due to their coordination abilities, facile syntheses, easily tunable steric factors, electronic properties and good solubility in common solvents.[1-4] Transition metal complexes with oxygen and nitrogen donor Schiff bases (O,N-ligands) are of particular interest[1-4] because of their ability to possess unusual configurations and to be structurally labile. The Fe(III), Co(III), Ni(II), Zn(II), Cd(II) and lanthanide(III) complexes with ONN-ligand synthesized by reaction of 2-pyridincarboxaldehyde and substituted aminophenols[5] have been obtained and investigated.[6] Some of them can be used as photoactive materials.[6-12] In a series of papers it have been shown that the iminophenol derivatives synthesized by condensation of *o*-aminophenols with various substituted aldehydes can undergo the intramolecular cyclization to give five- or six-membered rings[13-16] opening in alkaline solution in presence of metal ion.[17]
Recently we have described the synthesis of iminoketone[18], which can act as carbonyl reagent in condensation reactions with substituted *o*-aminophenols. In this case the resulting products features hydroxyl group and sterically hindered N=C-C=N fragment. Such compounds may be used as either neutral or valent bonded ligands.

Results and discussion

This study is aimed to the synthesis of the new sterically hindered ONN-ligand derived from the interaction of 3-(2,6-diisopropylphenylimino)butan-2-one with 2-amino-4,6-di-tert-butylphenol and the investigation of the properties of obtained compound. The treatment of 3-(2,6-diisopropylphenylimino)-butan-2-one with the *o*-aminophenol leads to the colorless crystalline solid compound identified as dihydrobenzoxazole **I** by the spectral methods, ^{15}N-^{1}H 2D *ge*-HSQC NMR spectrum and the X-ray structural analysis (Fig. 1). Compound **I** is the product of intramolecular cyclization of the desired N-substituted *o*-iminophenol (Scheme 1).



Scheme 1 The synthesis of compound **I.**

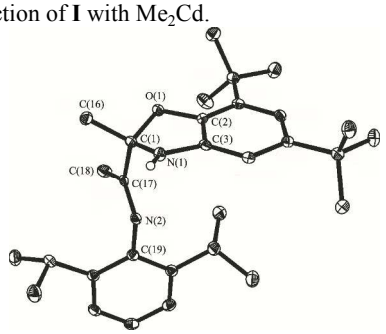


Fig.1 The molecular structure of **I**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except bonded to N(1)) are omitted for clarity. Selected distances [Å] and angles [°]: C(1)-O(1) 1.464(3), C(1)-N(1) 1.464(3), C(2)-O(1) 1.393(3), C(3)-N(1) 1.409(3), C(1)-C(16) 1.514(3), C(1)-C(17) 1.534(3), C(17)-C(18) 1.500(3), C(17)-N(2) 1.276(3), N(2)-C(19) 1.423(3), C(1)-O(1)-C(2) 105.7(2), C(1)-N(1)-C(3) 105.2(2), C(17)-N(2)-C(19) 122.0(2).

As we have mentioned above the *o*-iminophenols based on *o*-aminophenols with various substituted aldehydes are in equilibrium with an isomeric cyclic form of ligands. We tried to indicate each form of **I** by ^{1}H NMR in various solvents, but unfortunately concentration of this form is too low to be detected by NMR. This fact displays that the equilibrium is shifted completely to the dihydrobenzoxazole. However, an interesting phenomenon took place in deuterium methanol solution of **I**.
The freshly prepared solution of compound **I** in CD_3OD features ^{1}H NMR typical for such compounds. However, within 3-5 minutes in solution the intensity of the C_{sp3}-CH_3 methyl group signal is greatly reduced (Fig. 2). In ^{13}C NMR spectrum signal of this methyl group is transformed into a multiplet (Fig. 3).
The decreasing of the methyl group signal intensity and arising of multiplet in ^{13}C NMR can be caused by methyl group deuteration. The fact of selective deuteration of OH and NH groups in methanol-d4 and some other NMR solvents is widely known but selective deuteration of the methyl group in mild conditions is absolutely unusual.
Supposed H-D exchange can be explained by cyclization - decyclization equilibrium in solution (Scheme 2). The hydroxyl of **I*** is rapidly deuterated in CD_3OD forming OD group. Subsequently, deuterium of OD group migrates into methyl group forming a partially deuterated CH_2D group and then CHD_2 group up to fully deuterated CD_3 group (compound **II**).

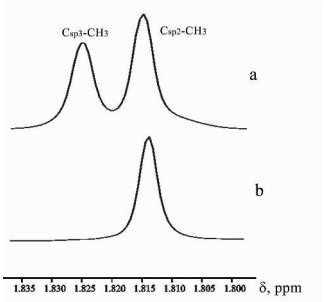


Fig. 2 Fragment of ^{1}H NMR spectrum of **I** in CD_3OD: a- freshly prepared solution; b- after 5 min.

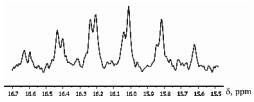
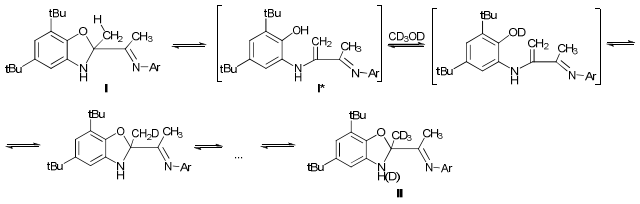


Fig.3 Fragment of ^{13}C NMR spectrum of **I** in CD_3OD after 5 min.



Scheme 2 The deuteration process in CD_3OD solution.

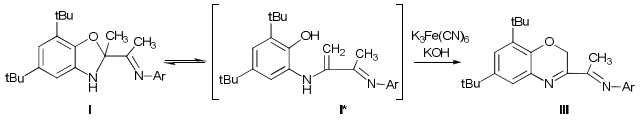
It should be noted that the peak of NH group is still present in the ^{1}H NMR spectrum while the C_{sp3}-CH_3 methyl group signal is completely disappear.

After a three-time recrystallization of **I** in CD_3OD the selectively deuterated product **II** was isolated. The deuteration degree is proven by absence of the methyl group signal in ^{1}H NMR spectrum. There are three signals observed in ^{2}H NMR spectrum of compound **II**. The chemical shift of the most intensive signal assigned to CD_3 group (1.80 ppm) is close to the chemical shift of the methyl protons in source compound **I** (1.83 ppm). The intensity of ^{2}H signals of CHD_2 (1.81 ppm) and CH_2D (1.82 ppm) groups are substantially lower.

The mass spectrum of **II** showed peaks both for the molecular ion at m/z = 451 and the ion corresponding to fragment of the molecule containing benzoxazole rings (m/z = 249) while the source compound **I** shows peaks at m/z=449 (M^+) and 246.

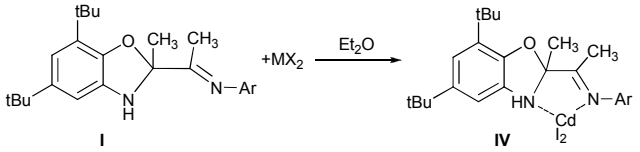
Taking into account the reaction conditions, the multiplicity of methyl signal in ^{13}C NMR and the intensity of residual methyl protons in ^{1}H NMR spectra we may affirm that the deuteration mostly leads to product with completely deuterated methyl group.

Another evidence of the existence of enamine form **I*** in solution is the oxidation of **I** by alkaline solution of potassium ferricyanide (Scheme 3). In this case C_{sp3}-Me group undergoes oxidation and the benzoxazine derivative **III** is formed. This reaction is possible due to the ring opening of **I** with formation of **I*** intermediate.



Scheme 3 The synthesis of compound **III.**

The coordination abilities of the ligand **I** have been investigated. It is known that the neutral complexes of R-DAB (N,N'-disubstituted diazabutadienes) are prepared by mixing of metal salt with the R-DAB ligand in stoichiometric molar ratio.[19] In our case the interaction of ligand **I** with cadmium iodide results in formation of colorless powder of metal complex **IV** (Scheme 4).



Scheme 4 The synthesis of compound **IV.**

The signals shifting in NMR spectrum of obtained complex **IV** in comparison with source ligand **I** indicates the electron density displacement from organic ligand to metal atom and formation of molecular complex L*CdI_2 (L = **I**). In this case **I** acts as a neutral ligand coordinated by two nitrogen atoms.

The structure of **IV** has been determined by single-crystal X-ray diffraction (Fig.4). Cadmium atom in **IV** is in distorted tetragonal coordination environment with two nitrogen and two iodide atoms on the tops. Dihedral angle between two aromatic rings is slightly more than observed for the parent ligand **I** (86.0°) amounts to 88.7°. The distances Cd(1)-N(1) (2.347(1) Å) and Cd(1)-N(2) (2.297(2) Å) are shorter than the sum of Van-der-Waals radii of cadmium and nitrogen atoms (3.7 Å), and are slightly more than the sum of covalent radii of these atoms (2.1 Å[20]). So the Cd-N distances are in the typical range of donor-acceptor bond lengths between aforementioned atoms. The bond lengths C(15)-O(1) (1.456(2) Å), C(15)-N(1) (1.469(2) Å) and C(17)=N(2) (1.275(2) Å) in ligand are in the range expected for organic compounds.

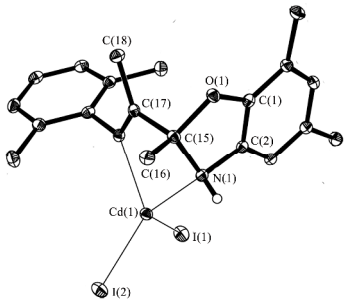
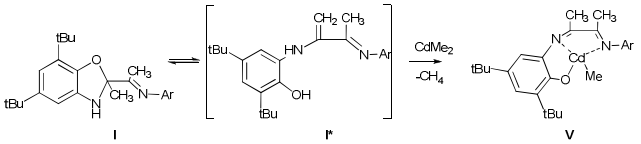


Fig.4 The molecular structure of **IV**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except bonded to N(1)) and Me-fragments of iPr-, tBu-groups are omitted. Selected distances [Å] and angles [°]: Cd(1)-N(1) 2.347(1), Cd(1)-N(2) 2.297(2), Cd(1)-I(1) 2.6714(2), Cd(1)-I(2) 2.7132(2), O(1)-C(1) 1.393(2), O(1)-C(15) 1.456(2), N(1)-C(2) 1.451(2), N(1)-C(15) 1.469(2), C(1)-C(2) 1.378(2), C(15)-C(17) 1.543(2), C(15)-C(16) 1.512(2), C(17)-C(18) 1.494(3), N(2)-C(17) 1.275(2), N(2)-C(19) 1.453(2), I(1)-Cd(1)-I(2) 120.395(2), N(1)-Cd(1)-N(2) 71.48(5), C(1)-O(1)-C(15) 104.5(1), C(2)-N(1)-C(15) 102.3(1), C(17)-N(2)-C(19) 120.1(2).

In spite of **I** has cyclic structure in solid state methyl group deuteration in CD_3OD solution means that the open form (**I***) containing phenol group is present in solution.

The interaction of **I** with equimolar amount of dimethylcadmium in ether solution leads to cadmium phenolate derivative **V**. The reaction is accompanied with solution color change and release of

methane. After cooling of the reaction mixture the deep brown crystals **V** were isolated with yield 82% (Scheme 5).



Scheme 5 The synthesis of compound **V.**

The molecular structure of **V** is depicted in Figure 5. According to X-Ray data analysis **V** adopts a dimeric structure with two cadmium cations bounded by two bridging oxygen atoms. The Cd(1) is in distorted tetragonal pyramidal environment: O(1), N(1), N(2) and C(61) form the base while O(2) occupies an apical site. The Cd(2) is in distorted tetrahedron environment with the O(1), O(2), N(3) and C(62) in the tops. The Cd(1), O(1), Cd(2) and O(2) form a distorted rhombus. The Cd(1)-O(1) (2.374(3) Å) and Cd(2)-O(2) (2.225(3) Å)[21,22] distances are significantly shorter than bonds Cd(1)-O(2) and Cd(2)-O(1) (2.398(3) Å and 2.240(2) Å) which have donor-acceptor nature. Also these distances are shorter than the sum of covalent radii of these atoms. Values of Cd(1)-N(1) (2.344(3) Å), Cd(1)-N(2) (2.428(4) Å) and Cd(2)-N(3)(2.578(3) Å) lie in the range typical for donor-acceptor bond lengths of aforementioned atoms. The cadmium atoms separated from each other by 3.370(4) Å. The distance between Cd(2) and N(4) atoms is 5.305(3) Å. This fact demonstrates that the N(4) atom is not coordinated on metal atom.

In accordance to X-ray analysis ligands in dimer **V** are not identically coordinated. However there is only one set of signals belonging to the ligand in ^{1}H NMR spectrum. The above data may be caused by either dissociation of **V** in solution or the coordination sphere dynamics.

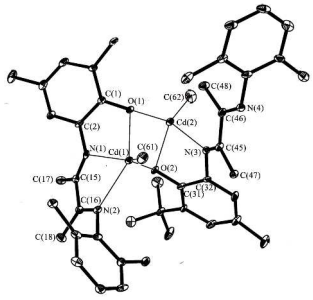
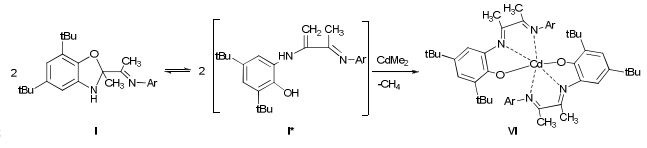


Fig.5 The molecular structure of **V**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and Me-fragments of iPr-, tBu-groups are omitted. Selected distances [Å] and angles [°]: Cd(1)-O(1) 2.374(3), Cd(1)-N(1) 2.344(3), Cd(1)-N(2) 2.428(4), Cd(1)-C(61) 2.146(4), Cd(2)-O(2) 2.225(3), Cd(2)-N(3) 2.578(3), Cd(2)-C(62) 2.146(5), O(1)-C(1) 1.325(5), C(1)-C(2) 1.434(6), N(1)-C(2) 1.402(5), N(1)-C(15) 1.289(5), N(2)-C(16) 1.274(5), N(2)-C(19) 1.441(5), C(1)-C(2) 1.434(6), C(15)-C(16) 1.520(5), C(15)-C(17) 1.508(6), C(16)-C(18) 1.507(6), O(2)-C(31) 1.361(5), N(3)-C(32) 1.434(6), N(3)-C(45) 1.285(5), N(4)-C(46) 1.271(5), N(4)-C(49) 1.426(5), C(31)-C(32) 1.406(6), C(45)-C(46) 1.500(6), C(45)-C(47) 1.517(5), C(46)-C(48) 1.514(5), O(1)-Cd(1)-N(1) 62.7(1), N(1)-Cd(1)-N(2) 68.2(1), O(2)-Cd(2)-N(3) 67.9(1), O(1)-Cd(1)-O(2) 78.6(1), O(1)-Cd(2)-O(2) 85.2(2).

The interaction of Me_2Cd with **I** (molar ratio 1:2) leads to the formation of deep blue derivative **VI** (Scheme 6).



Scheme 6 The synthesis of compound **VI.**

The ^{1}H and ^{13}C NMR spectra of **VI** demonstrate one set of signals belonging to the ligand.

The X-Ray analysis of **VI** shows that the phenolate ligands with diazabutadiene fragments are identically coordinated (Fig.6). The Cd(1) is in distorted octahedral environment. The N(1), N(3), N(4) and O(2) form the base while O(1) and N(2) occupy an apical sites. The *o*-aminophenolate fragments are plane and the dihedral angle between ones amounts 84.9°. The rings of aniline fragments of the ligand are almost parallel to each other. Dihedral angle between ones is 18.4°. The Cd(1)-O(1) (2.258(1) Å) and Cd(1)-O(2) (2.262(1) Å) distances are significantly shorter than bonds Cd-O which have donor-acceptor nature. These distances are comparable with Cd-O bonds lengths observed for the cadmium phenolate compounds.[21,22] Values of Cd-N distances (Cd(1)-N(1) 2.333(1), Cd(1)-N(2) 2.397(1), Cd(1)-N(3) 2.318(1) and Cd(1)-N(4) 2.317(1) Å) lie in the range typical for donor-acceptor bond nature between aforementioned atoms. The distances C-C and C-N (C(15)-C(16) 1.510(2) Å, C(45)-C(46) 1.510(2) Å, N(1)-C(15) 1.286(2) Å, N(2)-C(17) 1.286(2) Å, N(3)-C(45) 1.289(2) Å and N(4)-C(46) 1.295 Å) are corresponded to bond orders of one and two, respectively.

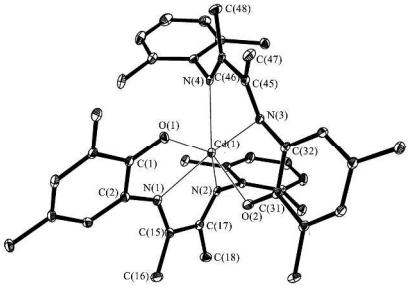


Fig.6 The molecular structure of **VI**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and Me-fragments of iPr-, tBu-groups are omitted. Selected distances [Å] and angles [°]: Cd(1)-O(1) 2.258(1), Cd(1)-O(2) 2.262(1), Cd(1)-N(1) 2.333(1), Cd(1)-N(2) 2.397(1), Cd(1)-N(3) 2.318(1), Cd(1)-N(4) 2.371(1), O(1)-C(1) 1.299(3), N(1)-C(2) 1.404(2), N(1)-C(15) 1.286(2), N(2)-C(17) 1.286(2), N(2)-C(19) 1.450(1), C(1)-C(2) 1.438(2), C(15)-C(16) 1.510(2), C(15)-C(17) 1.500(2), C(16)-C(18) 1.502(2), O(2)-C(31) 1.301(2), N(3)-C(32) 1.404(2), N(3)-C(45) 1.289(2), N(4)-C(46) 1.295(2), N(4)-C(49) 1.444(2), C(31)-C(32) 1.430(2), C(45)-C(46) 1.510(2), C(45)-C(47) 1.498(2), C(46)-C(48) 1.495(2), O(1)-Cd(1)-N(1) 72.14(4), N(1)-Cd(1)-N(2) 70.34(5), O(2)-Cd(1)-N(3) 72.48(4), N(3)-Cd(1)-N(4) 70.41(5), O(1)-Cd(1)-O(2) 96.46(4).

Conclusions

In the present work we have described the synthesis of novel ligand - benzoxazole **I**. It is shown that obtained compound **I** undergoes a ring open process to form the enamine species in solution. The coordination abilities of **I** have been studied. The ligand **I** is shown to demonstrate a neutral coordination type in complex with cadmium halide. A convenient procedure for the

synthesis of cadmium complexes with the new sterically hindered ONN- ligand has been developed. This method may be used for a synthesis of the simillar complexes containing different metals.

Experimental

General

2-amino-4,6-di-tert-butylphenol was prepared according to a previously described procedures.[23] Solvents were purified by standard methods.[24] All synthesis have been conducted in evacuated ampoules.

The NMR spectra were recorded on a «Bruker Avance III» NMR spectrometer (400 MHz) using $CDCl_3$, CD_3OD or C_6D_6 as the solvents and tetramethylsilane as the internal standard. IR-spectra were recorded by 'Specord M-80. Elemental analyses were obtained on "EuroEA-3028-HT". Mass spectra was recorded on mass spectrometer "Polaris Q" with ion trap mass analiser. Electron impact mass spectra (70 eV) were registrated in the mass range 50-550 m/e.

X-Ray crystallographic study of I, IV-VI

The X-ray data were collected on a Smart Apex diffractometer (for **I** and **IV**, graphite-monochromated, *MoKa*-radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K) and a Agilent Xcalibur E diffractometer (for **V** and **VI**, graphite-monochromated, *MoKa*-radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K). The structures were solved by direct methods and were refined on F^2 using *SHELXTL*[25] (**I** and **IV**) and *CrysAlis Pro*[26] (**V** and **VI**) package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. H1A in **I** was also found from Fourier syntheses of electron density, but were refined isotropically. All other hydrogen atoms were placed in calculated positions and were refined in the riding model. *SADABS*[27] (**I** and **IV**) and *ABSPACK* (*CrysAlis Pro*)[26] (**V** and **VI**) were used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection and refinement data are shown in Table 1 and corresponding cif files are available as supporting information. CCDC-772231 (**I**), 957572 (**IV**), 957573 (**V**), 957574 (**VI**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

Synthesis

N-(1-(5,7-di-tert-butyl-2-methyl-2,3-dihydrobenzo[d]-oxazol-2-yl)ethylidene)-2,6-diisopropylaniline (I)

A solution of 2-amino-4,6-di-tert-butylphenol (0.34 g, 15 mmol) in methanol (30 mL) was added to 3-(2,6-diisopropylphenylimino)butan-2-one (0.38 g, 1.6 mmol) in an evacuated ampoule. Reaction mixture was heated at 50 ºC during 10-15 min. Upon concentration of reaction mixture to 15-20 mL colorless crystals are formed.

Yield: 0.57 g (85%); m.p. = 82 ºC. m/z 448 (M^+, 100%); 449(M^++1, 33); 450(M^++2, 6). Found (%): C, 80.4; H, 9.9. Calculated for $C_{30}H_{44}N_2O$ (%): C, 80.3; H, 9.9. IR (nujol, ν/cm^{-1}): 3291br, 3062m, 1914w, 1857w, 1796w, 1666s, 1624w, 1605m, 1418s, 1365s, 1327m, 1300m, 1266m, 1224s, 1193s, 1105s, 1079s, 1029w, 1014w, 938w, 911w, 892m, 854s, 823m, 796w, 774s, 747m, 716m, 667m, 644w, 583w, 552w, 510w. ^{1}H NMR ($CDCl_3$, δ/ppm, J/Hz): 0.79 and 0.83 (both d, 6H, $(CH_3)_2CH$, J=6.88); 1.26 and 1.36 (both s, 9H, tBu); 1.83 and 1.86 (both s, 3H, Me); 2.23 and 2.64 (both sept, 1H, $(CH_3)_2CH$, J=6.88 Гц,); 5.88 (s, 1H, NH); 6.74 (br s, 2H, H_{arom}); 7.02-7.14 (m, 3H, H_{arom}). ^{1}H NMR (CD_3OD, δ/ppm, J/Hz): 0.81 and 0.85 (both d, 3H, $(CH_3)_2CH$, J=6.88); 1.13 and 1.16 (both d, 3H, $(CH_3)_2CH$, J=6.88); 1.27 and 1.35 (both s, 9H, tBu); 1.81 and 1.83 (both s, 3H, Me); 2.31 and 2.69 (both sept, 1H, $(CH_3)_2CH$, J=6.88 Гц); 4.57 (s, 1H, NH); 6.73 and 6.75 (both d, 1H, H_{arom}, J=7.26 Гц); 6.98-7.17 (m, 3H, H_{arom}). ^{13}C NMR ($CDCl_3$, δ/ppm): 15.4, 22.3, 22.7, 22.8, 23.0, 23.2, 24.8, 27.9, 28.2, 29.7, 31.8, 34.0, 34.6, 76.7, 77.0, 77.3, 100.5, 107.4, 115.0, 122.9, 123.0, 123.8, 130.8, 135.7, 136.0, 138.0, 144.2, 144.7, 144.9, 171.7 (C=N). ^{13}C NMR (CD_3OD, δ/ppm): 14.4; 21.5; 21.8; 22.0; 22.2; 27.6; 27.9; 29.0; 30.9; 33.6 (CH_3); 34.1 (CH_3); 100.3; 107.1; 114.5; 122.6; 123.7; 130.5; 135.5; 135.8; 138.1; 144.1; 144.7; 144.9; 172.0 (C=N). The crystals of **I** suitable for X-ray were obtained from CH_3CN.

N-(1-(6,8-di-tert-butyl-2H-benzo[1,4]oxazin-3-yl) ethylidene)-2,6-diisopropylaniline (III)

A solution of **I** (0.5 g., 1.1 mmol) in 15 mL of diethyl ether and the alkaline solution of potassium ferricyanide (1 g. $K_2Fe(CN)_6$, 0.1 g. KOH in 50 mL of water) were stirred 24 hours with a magnetic stirrer until **I** disappeared. Then the organic layer was separated and dried by $MgSO_4$. The ether was removed and the crude product was dissolved in acetonitrile. After cooling the yellow needle crystals were formed.

Yield: 0.43 g (86%). m.p. 167˚C. Found (%): C, 80.7; H, 9.5. Calculated for $C_{30}H_{42}N_2O$(%): C, 80.9; H, 9.3. IR (nujol, ν/cm^{-1}): 1627m, 1589w, 1360s, 1315m, 1258m, 1243m, 1217m, 1089w, 1021m, 976w, 938w, 912w, 882m, 826w, 792w, 762s, 720w, 698w, 679w, 653w. ^{1}H NMR ($CDCl_3$, δ/ppm, J/Hz): 1.14 and 1.15 (both d, 6H, $CH(CH_3)_2$, J=6.88); 1.34 (s, 9H, tBu); 1.41 (s, 9H, tBu); 2.07 (s, 3H, CH_3); 2.63 (sept, 2H, $CH(CH_3)_2$, J=6.88); 5.12 (s, 2H, CH_2); 7.08-7.34 (m, 5H, H_{arom}). ^{13}C NMR ($CDCl_3$, δ/ppm): 15.7; 22.7; 23.2; 28.3; 29.7; 31.5; 34.4; 34.7; 61.2 (CH_2); 123.0; 123.2; 124.0; 124.6; 133.9; 135.2; 137.2; 143.6; 144.2; 145.8; 159.1 and 166.15 (C=N).

(N-(1-(5,7-di-tert-butyl-2-methyl-2,3-dihydrobenzo[d]oxazol-2-yl)ethylidene)-2,6-diisopropylaniline) cadmium diiodide (IV)

A solution of **I** (0.1 g, 0.2 mmol) in diethyl ether (25 mL) was added to a suspension of CdI_2 in Et_2O (10 mL). Reaction mixture was stirred at 20 ºC until cadmium iodide crystals disappeared. Hexane (30 mL) was added to the reaction solution and a colorless powder was formed after the ether evaporation.

Yield: 0.12 g (73%). Found (%): C, 44.2; H, 5.5; Cd, 13.7; I, 31.2. Calculated for $C_{34}H_{54}CdI_2N_2O_2$ (%): C, 44.2; H, 5.4; Cd, 13.8; I, 31.2. IR (nujol, ν/cm^{-1}): 3120s (N-H), 1646s (C=N), 1413s, 1364s, 1326w, 1270m, 1236m, 1179s, 1134s, 1115s, 1081s, 965s, 916m, 893s, 871s, 837m, 803m, 788s, 754m, 743m, 720w, 626w. ^{1}H NMR ($CDCl_3$, δ/ppm, J/Hz): 0.45 (d, 3H, $(CH_3)_2CH$, J=6.73); 0.96 (d, 3H, $(CH_3)_2CH$, J=6.73); 1.19 (d, 3H, $(CH_3)_2CH$, J=6.73); 1.25 (d, 3H, $(CH_3)_2CH$, J=6.73); 1.33 (s, 9H, tBu); 1.35 (s, 9H, tBu); 1.96 (sept, 1H, $(CH_3)_2CH$, J=6.73); 2.04 (s, 3H, CH_3); 2.37 (s, 3H, CH_3); 2.86 (sept, 1H, $(CH_3)_2CH$, J=6.73);

Table1. The crystal data collection and structure refinement data for the complexes **I**, **VI-VI**.

	I	**IV**	**V**	**VI**
Formula	$C_{30}H_{44}N_2O$	$C_{34}H_{54}CdI_2N_2O_2$	$C_{68.20}H_{107.50}Cd_2N_4O_{3.55}$	$C_{64}H_{96}CdN_4O_3$
M_r	448.67	888.99	1265.08	1081.85
Crystal size, mm³	0.15×0.10×0.05	0.42×0.14×0.12	0.40×0.10×0.10	0.40×0.20×0.20
Crystal system	*Triclinic*	*Monoclinic*	*Triclinic*	*Monoclinic*
Space group	*P-1*	*P2(1)/n*	*P-1*	*P2(1)/n*
a, Å	11.2464(9)	19.3052(6)	12.7219(2)	15.0475(3)
b, Å	15.861(1)	11.9215(4)	17.4042(4)	26.8007(4)
c, Å	18.527(1)	19.4653(7)	17.4215(4)	16.0102(3)
α, °	102.754(2)	90	72.473(2)	90
β, °	107.317(2)	119.466(1)	78.284(2)	109.913(2)
γ, °	109.440(2)	90	73.561(2)	90
Cell volume, Å	2781.0(4)	3900.4(2)	3498.5(1)	6070.6(2)
Z	4	4	2	4
D_{calc}, *g/cm³*	1.072	1.514	1.201	1.184
μ, *mm⁻¹*	0.064	2.171	0.652	0.405
F_{000}	984	1768	1338	2320
2θ range, °	52	52	52	52
Index ranges	$-13 \le h \le 13$	$-23 \le h \le 23$	$-15 \le h \le 15$	$-18 \le h \le 18$
	$-19 \le k \le 19$	$-14 \le k \le 14$	$-21 \le k \le 21$	$-33 \le k \le 33$
	$-22 \le l \le 22$	$-23 \le l \le 24$	$-21 \le l \le 21$	$-19 \le l \le 19$
Reflns collected	23923	32685	53781	92898
Independent reflns	10872	7604	13581	11878
R_{int}	0.0452	0.0211	0.0674	0.0907
Completness to θ	99.6	99.4	98.7	99.6
Data /restraints /parameters	10872 / 0 / 619	7604 / 0 / 388	13581 / 45 / 736	11878 / 7 / 688
GooF	1.038	1.026	1.053	1.033
R_1 *(I>2σ(I))*	0.0667	0.0229	0.0748	0.0392
wR_2 *(all data)*	0.1528	0.0566	0.1943	0.1020

4.85 (br s, 1H, NH); 7.04-7.25 (m, 5H, H_{arom}). ^{13}C NMR ($CDCl_3$, δ/ppm): 17.98; 23.23; 23.77; 23.80; 24.15; 26.30; 28.22; 28.30; 29.91; 31.72; 34.42; 35.15; 100.54; 115.50; 121.96; 124.26; 124.43; 127.24; 131.15; 132.67; 138.08; 138.57; 140.12; 146.04; 146.28; 180.36 (C=N). The crystals of **IV** suitable for X-ray were obtained from Et_2O.

Methyl cadmium (2,4-di-tert-butyl-6-(3-(2,6-diisopropyl phenylimino)butan-2-ylidene)aminophenolate (V)

Me_2Cd (0.284g, 2 mmol) was added to a solution of **I** (0.898 g, 2mmol) in diethyl ether (30 mL). The color change from colorless to deep brown took place immediately. Red-brown crystals were isolated after cooling.

Yield: 1.024 g (89%). Found (%): C, 64.8; H, 8.0; Cd, 19.6. Calculated for $C_{31}H_{46}CdN_2O$ (%): C, 64.7; H, 8.1; Cd, 19.6. ^1H NMR ($CDCl_3$, δ/ppm, J/Hz): -0.69 (m, 3H, CH_3Cd, $J_{H\text{-}Cd}$ = 82.47); 1.12 (d, 6H, $(CH_3)_2CH$, J=6.86); 1.15 (d, 6H, $(CH_3)_2CH$, J=6.86); 1.35 (s, 9H, tBu); 1.50 (s, 9H, tBu); 2.17 (s, 3H, CH_3); 2.60 (sept, 2H, $(CH_3)_2CH$, J=6.86); 2.64 (s, 3H, CH_3); 6.87(d, 1H, H_{arom}, J=2.48); 7.17-7.21 (m, 3H, H_{arom}); 7.32 (d, 1H, H_{arom}, J=2.48). ^{13}C NMR ($CDCl_3$, δ/ppm): -13.65 (CH_3Cd); 19.32; 23.75; 28.47; 29.55; 31.66; 34.00; 35.39; 115.65; 123.75; 124.83; 129.90; 131.44; 133.53; 137.47; 139.83; 142.50; 159.06 (C=N); 162.73 (C_{arom}-N); 167.48 (C=N). The crystals of **V** suitable for X-ray were obtained from Et_2O.

Cadmium bis(2,4-di-tert-butyl-6-(3-(2,6-diisopropylphenyl imino)butan-2-ylidene) aminophenolate (VI)

Me_2Cd (0.142 g, 1 mmol) was added to a solution of **I** (0.898 g, 2 mmol) in diethyl ether (30 mL). The color change from colorless to deep blue took place immediately. Blue crystals were isolated after cooling.

Yield: 0.84 g (83%). Found (%): C, 71.6; H, 8.6; Cd, 11.2.

Calculated for $C_{60}H_{86}CdN_4O_2$ (%): C, 71.5; H, 8.6; Cd, 11.2. IR (nujol, v/cm^{-1}): 1618w, 1589w, 1556s, 1522m, 1506s, 1411m, 1373s, 1361s, 1325s, 1299m, 1278s, 1254s (C-O), 1189s, 1157s, 1121s, 1056w, 1024w, 979s, 935w, 908m, 870m, 837s, 793m, 781s, 734m, 704w, 645w, 633w, 597w, 583s, 553w, 512w, 485m. ^{1}H NMR (C_6D_6, δ/ppm, J/Hz): 0.30 (d, 3H, $(CH_3)_2CH$, J=6.81); 0.85 (d, 3H, $(CH_3)_2CH$, J=6.81); 1.08-1.10 (m, 6H, $(CH_3)_2CH$, J=6.81); 1.36 (s, 9H, tBu); 1.54 (s, 9H, tBu); 1.64 (s, 3H, CH_3); 2.36 (sept, 1H, $(CH_3)_2CH$, J=6.81); 2.41 (s, 3H, CH_3); 3.58 (sept, 1H, $(CH_3)_2CH$, J=6.81); 6.96 (d, 1H, H_{arom}, J=2.22); 6.87-7.03 (m, 3H, H_{arom}); 7.44 (d, 1H, H_{arom}, J=2.22). ^{13}C NMR (C_6D_6, δ/ppm): 19.50; 19.82; 22.75; 23.01; 24.11; 24.32; 27.39; 28.02; 29.58; 31.61; 33.82; 35.51; 116.69; 123.43; 124.53; 125.36; 125.86; 129.88; 130.54; 137.79; 139.13; 139.87; 145.13; 150.16; 165.68 (C=N); 171.68 (C=N). The crystals of **VI** suitable for X-ray were obtained from Et_2O.

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The novel benzoxazole **I** undergoes a fast intramolecular decyclization and demonstrates either a neutral or anionic coordination type in cadmium complexes.