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# Chemical and Electrochemical Syntheses of the Binuclear Zinc and Cadmium Chelates Based on the Sterically Hindered Schiff Bases

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**Abstract**—Chemical and electrochemical syntheses of a series of the zinc(II) and cadmium(II) complexes were carried out on the basis of sterically hindered Schiff bases, which are the condensation products of 4,6-di-*tert*-butyl-2-aminophenol with the salicylaldehyde derivatives ($H_2L$, $H_2L^1$). The structures and compositions of the synthesized binuclear complexes $M_2L_2$ and $M_2L^1_2$, where M = Zn(II) and Cd(II), were proved by the data of elemental analysis, IR spectroscopy, and $^1H$ NMR spectroscopy. The structures of the $Zn_2L_2 \cdot 2Py$ and $Zn_2L_2 \cdot 2DMF$ dimers were proved by X-ray diffraction analysis. The electrochemical dissolution of zero-valence zinc and cadmium in methanol in the presence of equimolar amounts of $H_2L$ and $H_2L^1$ made it possible to isolate dimeric complexes of the corresponding metals of the composition $M_2L_2$ and $M_2L^1_2$.

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## INTRODUCTION

Although the active study of the complexation ability of the tridentate Schiff bases has been started as early as in the middle of the XX century [1, 2], these compounds are presently among the main objects of the coordination chemistry section dealing with metallochelate derivatives. This is caused first by a variety of possible structures formed depending on the synthesis conditions and the electronic structure of the complexing metal (a–e) [3–14]. In addition, complexes based on the tridentate Schiff bases are recently considered as potential magnetoactive [15–17], catalytic [18–20], and optical materials [21, 22].

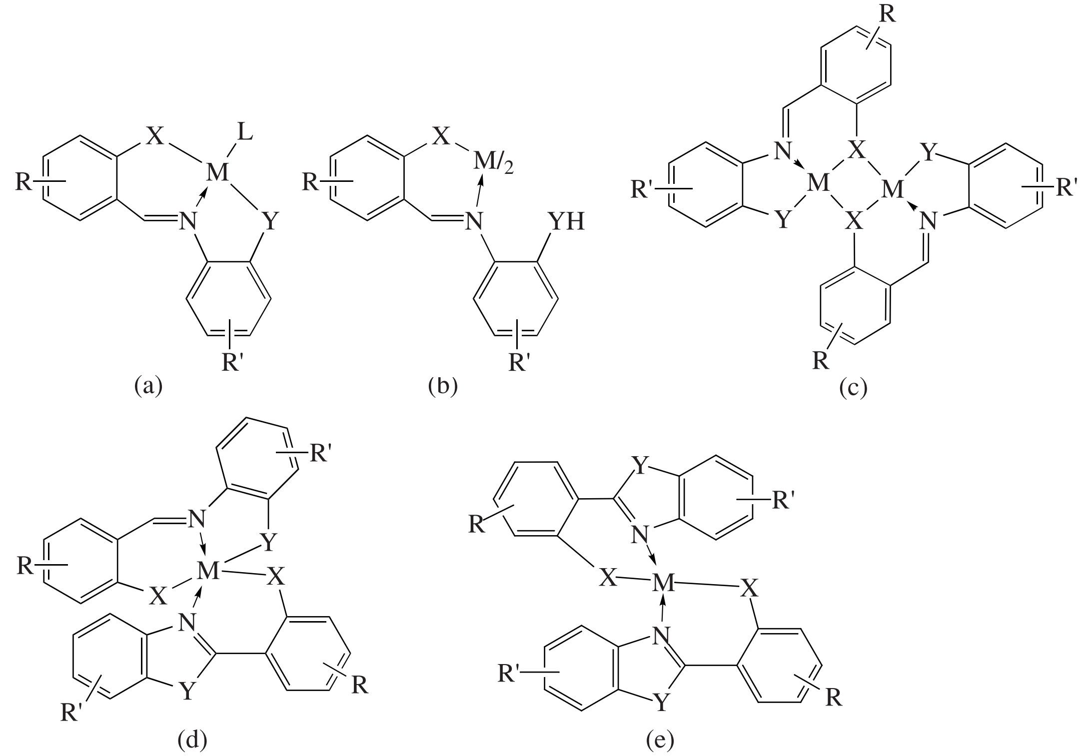
The present study is devoted to the synthesis and studies of the physicochemical properties and structures of the binuclear zinc(II) and cadmium(II) chelates based on sterically hindered tridentate azomethines and to the comparison of the results of electrochemical and chemical methods of synthesis of the above metal complexes.

## EXPERIMENTAL

4,6-Di-*tert*-butyl-2-aminophenol synthesized according to a described procedure [23], as well as N-(3,5-di-*tert*-butyl-2-oxyphenyl)salicylaldimine ($H_2L$) and N-(3,5-di-*tert*-butyl-2-oxyphenyl-5-nitro)salicylaldimine ($H_2L^1$) synthesized according to a known procedure [24], were used.

**Chemical synthesis of the complexes.** An equimolar amount of the corresponding metal acetate (Zn(II), Cd(II)) dissolved in methanol was added to a boiling methanolic solution (15 ml) containing 0.001 mole of the corresponding azomethine ($H_2L$ and $H_2L^1$). After reflux for several hours, crystalline precipitates of the complexes formed upon cooling were filtered off, washed with hot isopropanol, and dried in vacuo.

**Electrosynthesis of the complexes** was carried out according to a standard procedure [4] in methanol using a platinum electrode as a cathode and metal plates (Zn and Cd) as anodes. A working methanolic solution (25 ml) contained 0.001 mole of the corresponding ligand ($H_2L$, $H_2L^1$) and 0.01 g of $Et_4NClO_4$ as a conducting additive. Electrolysis was carried out in a



X = O, S; Y = O, S, NR

U-shaped glass tube with unseparated anodic and cathodic spaces with a current strength of 10 mA and an initial voltage of 8 V for 2 h. After the end of electrolysis, precipitates of the complexes formed were filtered off, washed with hot isopropanol, and dried in vacuo.

The C,H,N-elemental analysis data and selected physicochemical characteristics of the synthesized complexes (**I–VIII**) are given in Table 1.

Single crystals of complexes **V** and **VI** suitable for X-ray diffraction were obtained on slow cooling of the reaction mixture.

**Table 1.** The Zn(II) and Cd(II) complexes with N-(3,5-di-*tert*-butyl-2-oxyphenyl)salicylaldimines ($H_2L$ and $H_2L^1$)

| Compound | Empirical formula | Content (found/calculated), % | | | Mp, °C | Yield,% (synthesis)* |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| $[Zn_2L_2]$ (**I**) | $C_{42}H_{50}N_2O_4Zn_2$ | 65.24/64.94 | 6.83/6.44 | 3.54/3.61 | >250 | 66 (C)<br>77 (EC)<br>12 (TEC) |
| $[Cd_2L_2]$ (**II**) | $C_{42}H_{50}N_2O_4Cd_2$ | 57.79/57.88 | 6.02/5.74 | 3.34/3.22 | >250 | 52 (X)<br>72 (EC)<br>9 (TEC) |
| $[Zn_2L^1_2]$ (**III**) | $C_{42}H_{48}N_4O_8Zn_2$ | 60.02/59.57 | 5.49/5.67 | 6.67/6.62 | >250 | 62 (C)<br>79 (EC)<br>11 (TEC) |
| $[Cd_2L^1_2]$ (**IV**) | $C_{42}H_{48}N_4O_8Cd_2$ | 52.91/52.45 | 5.19/4.99 | 5.67/5.83 | >250 | 59 (C)<br>74 (EC)<br>8 (TEC) |
| $[Zn_2L_2] \cdot 2Py$ (**V**) | $C_{52}H_{60}N_4O_4Zn_2$ | 66.54/66.81 | 6.22/6.42 | 6.24/5.99 | >250 | 88 |
| $[Zn_2L_2] \cdot 2DMF$ (**VI**) | $C_{48}H_{64}N_4O_6Zn_2$ | 61.97/62.35 | 6.87/6.93 | 5.84/6.06 | >250 | 93 |
| $[Zn_2L_2] \cdot 2DMSO$ (**VII**) | $C_{46}H_{62}N_2O_6S_2Zn_2$ | 58.74/59.23 | 6.51/6.65 | 3.14/3.00 | >250 | 87 |
| $[Zn_2L_2] \cdot 2$*iso*-PrOH (**VIII**) | $C_{48}H_{66}N_2O_6Zn_2$ | 64.73/64.29 | 7.29/7.37 | 2.97/3.13 | >250 | 89 |

* C is chemical, EC is electrochemical, and TEC is template electrochemical syntheses.

Elemental analysis for C, H, and N was carried out on a Carlo Erba Instruments TCM 480 instrument. IR spectra of samples were recorded on a Nicolet Impact-400 instrument in the range from 4000 to 400 cm$^{-1}$ (KBr pellets). Electronic absorption spectra were measured on a Varian Cary-100 spectrophotometer. Fluorescence spectra were obtained on a Varian Eclipse spectrofluorimeter. $^1$H NMR spectra were detected at the Research Institute of Physical and Organic Chemistry on a Varian UNITY-300 spectrometer in a DMSO-d$_6$ solution at 20°C using tetramethylsilane as an internal standard. The melting point was measured on the Kofler heating stage.

**X-Ray diffraction analyses** of compounds **V** and **VI** were carried out on a SMART APEX II CCD diffractometer (Mo$K_\alpha$ radiation, graphite monochromator, ω scan mode). The structures of compounds **V** and **VI** were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for $F^2_{hkl}$. Hydrogen atoms were located from difference electron density syntheses and refined in the isotropic approximation.

Selected crystallographic data and refinement parameters are given in Table 2. All calculations were performed by the SHELXTL PLUS program package [25]. The coordinates of atoms and other parameters for structure **I** were deposited with Cambridge Crystallographic Data Centre (nos. 729 702 (**V**) and 729 703 (**VI**); http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

Continuing the studies of the complexation ability of Co(II), VO(II), and Pd(II) with the tridentate Schiff bases (condensation products of sterically hindered *o*-aminophenol with salicylaldehydes [12–14]), we carried out the chemical and electrochemical syntheses and studied the structures of the zinc and cadmium complexes based on analogous ligating compounds.

As compared to the spectra of the noncoordinated ligands, in the IR spectra of complexes **I–IV** the bands of stretching vibrations of the OH group of the *o*-aminophenol fragment at 3620 cm$^{-1}$ disappear and the band of the ν(C=N) stretching vibrations exhibits the downfield shift by 11–16 cm$^{-1}$, indicating that the nitrogen atom of the C=N azomethine group participates in coordination with the metal.

The $^1$H NMR spectra (DMSO-d$_6$) of the zinc complexes (**I, III**) exhibit the disappearance of signals from the protons of the hydroxy groups ($\delta_{OH}$) of the amine and aldehyde fragments (in the $^1$H NMR spectra of the $H_2L$ and $H_2L^1$ ligands these signals appear at 12.0 and 8.8 ppm) and the downfield shift of the proton of the HC=N imino group by 0.3–0.6 ppm (for **I–VIII** with the following values: 8.52, 8.58, 8.54, 8.85, 8.68, 8.75, 8.63, and 8.62, respectively; in the $^1$H NMR spectra of $H_2L$ and $H_2L^1$ this signal was detected at 8.2 ppm). In addition to the above listed changes upon complex formation, the $^1$NMR spectra of cadmium complexes **II** and **IV** contain signals from the protons of the HC=N imino group (8.58 and 8.85 ppm) with the characteristic constants $^3J_{Cd\text{–}H} = 26.8$ Hz and $^3J_{Cd\text{–}H} = 27.3$ Hz, respectively, which additionally confirms that the coordination bond is localized on the nitrogen atom of the imino group of the ligands. Based on the spectral (NMR, IR) data, we can assume that the sterically hindered tridentate Schiff bases in the reactions with the Zn$^{2+}$ and Cd$^{2+}$ ions act in the dideprotonated form L$^{2-}$ and (L$^1$)$^{2-}$ and form binuclear complexes **I–IV** (type c).

**Table 2.** Selected crystallographic data and refinement parameters for structures **V** and **VI**

| Parameter | Value | |
|---|---|---|
| | **V** | **VI** |
| FW | 935.78 | 923.81 |
| *T*, K | 100 | 100 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| *Z* | 1 | 1 |
| *a*, Å | 9.4547(9) | 8.7264(9) |
| *b*, Å | 9.8691(8) | 9.4530(9) |
| *c*, Å | 14.1226(12) | 15.6197(17) |
| α, deg | 73.3753(17) | 81.906(3) |
| β, deg | 76.3533(17) | 83.069(2) |
| γ, deg | 71.3425(19) | 68.846(3) |
| V, Å$^3$ | 1181.10(18) | 1186.3(2) |
| $\rho_{calcd}$, g/cm$^{-3}$ | 1.316 | 1.293 |
| $\mu_{Mo}$, cm$^{-1}$ | 10.64 | 10.61 |
| *F*(000) | 492 | 488 |
| $2\theta_{max}$, deg | 89 | 56 |
| Number of measured reflections | 96565 | 8925 |
| Number of independent reflections | 18677 | 5741 |
| Number of reflections with $I > 2\sigma(I)$ | 15139 | 4779 |
| Number of refined parameters; | 400 | 399 |
| $R_1$ by reflections with $I > 2\sigma(I)$ | 0.0316 | 0.0331 |
| $wR_2$ by all independent | 0.0769 | 0.0803 |
| GOOF | 1.012 | 1.000 |
| $\rho_{max}/\rho_{min}$, *e* Å$^{-3}$ | 0.816/–0.505 | 0.489/–0.531 |

The compositions and structures of the metallochelates synthesized by the electrochemical method are identical to those for **I–IV** prepared by standard chemical procedures.

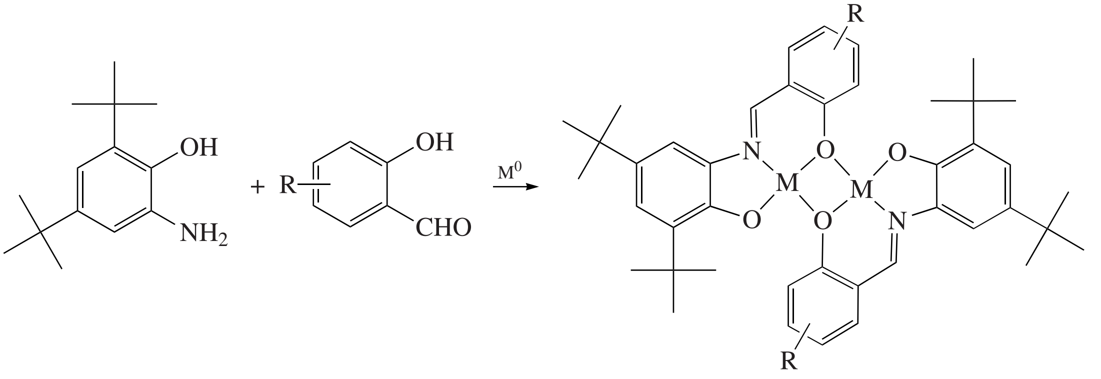
The total electrolysis process can be presented as follows:

$(–)Pt/CH_3OH + H_2L\ (H_2L^1)/M(+)$

Cathode: $H_2L\ (H_2L^1) + 2e \longrightarrow L^{2-}\ (L^1)^{2-} + H_2$;

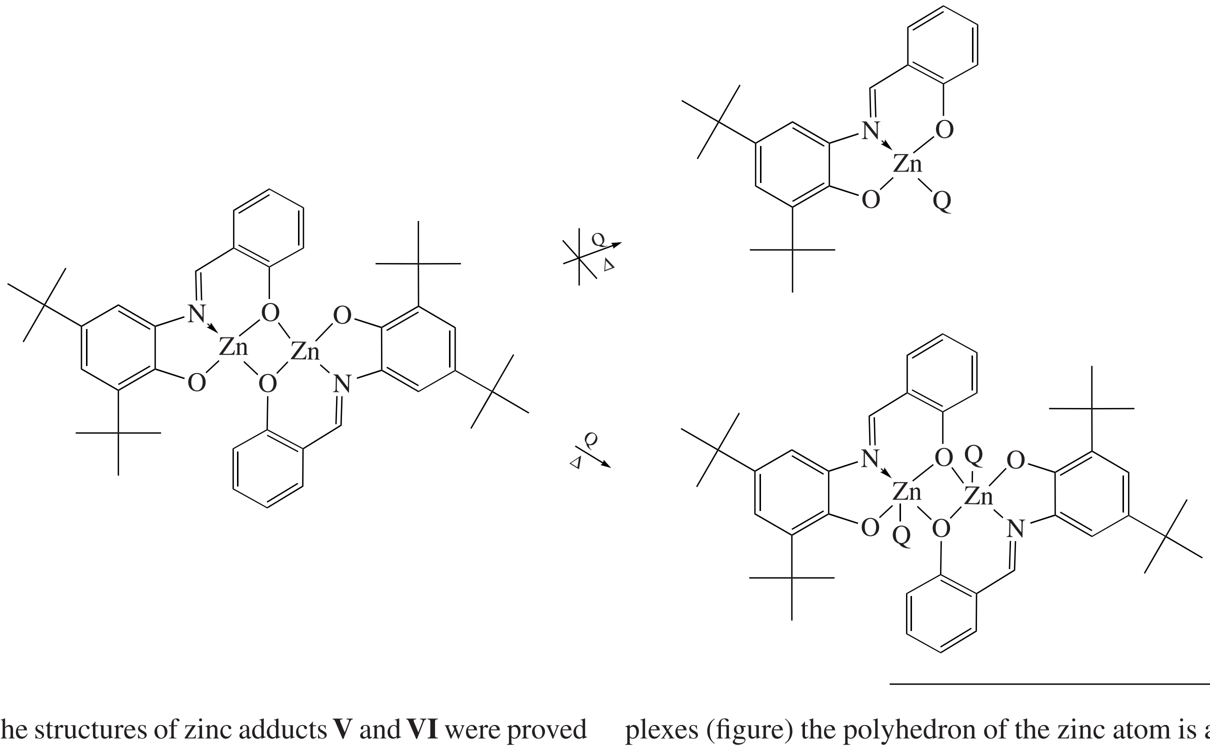
Anode: $2M\ (Zn, Cd) + 2L^{-}(L^1)^{2-} \longrightarrow M_2L_2\ (M_2L^1_2) + 4e$.

Template electrosynthesis [4] also affords the dimeric complexes in very low yields (Table 1), which is due to the redox processes that occur in the electrochemical cell via the scheme

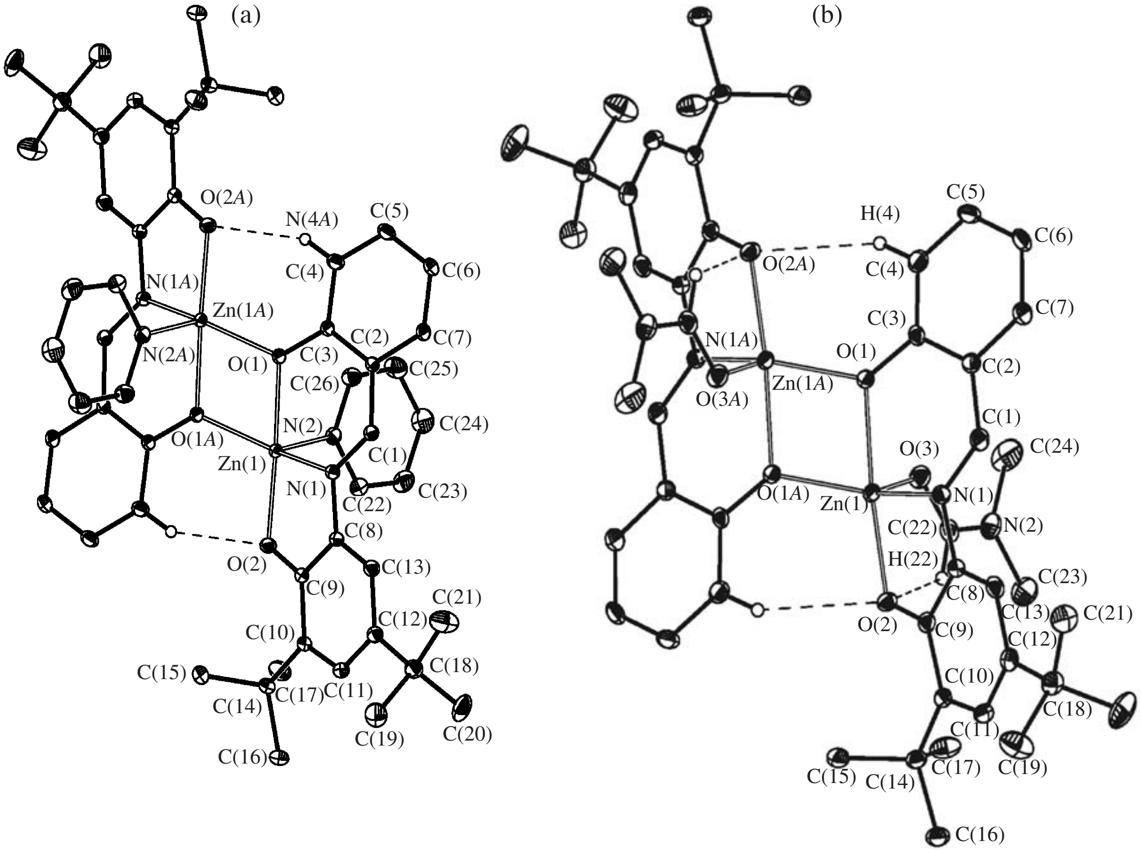


R = H, $NO_2$

Prolong (96 h) reflux of complex **I** in a medium of donor aprotic solvents (pyridine, DMF, and DMSO) and isopropanol in order to reveal a possibility of preparing mononuclear adducts of the tridentate Schiff bases [8] (type a) results in the isolation of the adducts of the binuclear complexes of the tridentate Schiff bases in which the metal is coordinated to the adduct-forming components, namely, solvent molecules, to form the coordination compounds $Zn_2L_2(L^1)_2Q_2$, where Q = Py (**V**), DMF (**VI**), DMSO, iso-PrOH (**V–VIII**).



The structures of zinc adducts **V** and **VI** were proved by X-ray diffraction analysis. The crystals of complexes **V** and **VI** are isomorphous, which makes it possible to correctly analyze the influence of the solvate molecule on the bond length redistribution. In centrosymmetric binuclear molecules of the both complexes (figure) the polyhedron of the zinc atom is a distorted trigonal bipyramid with the O(1) and O(2) atoms in the axial positions. Selected bond lengths and bond angles in the both complexes are similar (Table 3). In particular, for the bond involving the Zn atom the divergences do not exceed 0.02 Å, whereas for the bonds in



General view of complexes (a) **V** and (b) **VI** in the representation of atoms by thermal ellipsoids (50% probability).

the organic ligand they are comparable with the experimental errors (<0.003 Å). The main distinctions in structures of two complexes are observed for conformations of the ZnNC$_3$O six-membered metallocycles. In complex **V** this cycle is characterized by the sofa conformation (the Zn(1) atom deviates from the plane of other atoms by 0.73 Å), and complex **VI** is characterized by the half-chair conformation (the deviations of the Zn(1) and O(1) atoms from the NC$_3$ plane are 0.50 and –0.13 Å). The conformation of the ZnOC$_2$N five-membered cycle is the same in the both complexes. This conformation can be described as a strongly flattened envelope with the shift of the zinc atom by 0.037 and 0.17 Å (the root-mean-square deviation of other atoms does not exceed 0.006 Å) in complexes **V** and **VI**, respectively. In addition, in two Zn adducts the mutual arrangement of two ligands is different: the angle between the Zn(1)O(1)O(2)N(1) and Zn(1)O(2)Zn(1*A*) planes is 26.5° in **V** and 42.1° in **VI**. The greater bent of the molecule in complex **VI** weakens the intramolecular contactC(4)–H(4)···O(2*A*)compared to **V**, which appears as an increase in the corresponding H···O and C···O distances from 2.13 and 3.100(1) Å in **V** to 2.49 and 3.293(1) Å in **VI**. A possible reason for the variation of the conformation can be both the electronic factors (differences in the donor characteristics of pyridine and dimethylformamide) and additional C–H···O interactions formed by the DMF solvate molecule in crystal H(22)···O(2) 2.28, C···O 2.988(2) Å (figure).

The analysis of the crystal packing showed that in crystal **V** coordinated pyridine forms rather strong interactions C–H···π (C(8)–C(13) (1 – *x*, –*y*, –*z*) (H(24*A*)···C(8) 2.69, H(24*A*)···C(9) 2.56, H(24*A*)···C(10) 2.72 Å) joining the molecules into chains. The latter are joined in crystal due to the stacking interactions (C···C 3.225(1) Å) into a three-dimensional framework. Crystal **VI** contains many interactions C···C (3.31–3.34 Å) joining the molecules into layers.

The electronic absorption spectra of complexes **VI** and **VIII** in DMSO solutions are characterized by long-wavelength absorption bands with maxima at 377–453 nm and molar absorption coefficients at the maxima of 14700–24540 l mol$^{-1}$ cm$^{-1}$ depending on the ligand structure and the adduct-forming component. In DMSO solutions these compounds have fluorescence with band maxima at 577 nm regardless of the nature of the coordinated solvent.

Thus, the dimeric zinc and cadmium metallochelates were synthesized by the chemical and electrochemical methods. The adducts of the binuclear zinc and cadmium complexes based on the tridentate Schiff bases (derivatives of sterically hindered *o*-aminophe-

**Table 3.** Selected bond lengths and bond angles in complexes **V** and **VI**

| Bond | *d*, Å | |
|---|---|---|
| | **V** | **VI** |
| Zn(1)–O(1) | 2.0933(5) | 2.081(1) |
| Zn(1)–O(2) | 1.9851(5) | 1.995(1) |
| Zn(1)–N(1) | 2.0779(5) | 2.061(1) |
| Zn(1)–L* | 2.0981(6) | 2.056(1) |
| Zn(1)–O(1*A*) | 2.0011(5) | 1.984(1) |
| O(1)-C(3) | 1.3319(7) | 1.335(2) |
| O(2)–C(9) | 1.3232(7) | 1.324(2) |
| N(1)–C(1) | 1.2916(8) | 1.293(2) |
| N(1)–C(8) | 1.4138(8) | 1.415(2) |
| **Angle** | **ω, deg** | |
| O(1*A*)Zn(1)O(2) | 107.20(2) | 108.60(5) |
| O(2)Zn(1)N(1) | 81.48(2) | 81.89(5) |
| O(1*A*)Zn(1)N(1) | 146.03(2) | 134.33(6) |
| O(2)Zn(1)O(1) | 161.07(2) | 167.74(5) |
| O(1*A*)Zn(1)O(1) | 76.701(19) | 77.51(6) |
| N(1)Zn(1)O(1) | 85.50(2) | 86.31(5) |
| O(2)Zn(1)L* | 100.62(2) | 95.75(5) |
| LZn(1)N(1)* | 103.13(2) | 111.06(6) |
| LZn(1)O(1)* | 95.67(2) | 91.57(5) |
| O(1*A*)Zn(1)L* | 107.19(2) | 111.80(5) |
| Zn(1*A*)O(1)Zn(1) | 103.30(2) | 102.49(6) |

* L is N(2)(Py) in **V** and O(3)(DMF) in **VI**.

nol) were characterized for the first time. An advantage of the electrosynthesis is its “mild” conditions and higher (compared to the standard chemical procedure) yields of the final products.

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