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Cadmium(II) Complexes with Redox-Active Indophenol Ligands: Synthesis and Structures

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Abstract—The Cd(II) complexes with redox amphoteric 2,6-di-(*tert*-butyl)-4-((2-hydroxyphenyl)imino)cyclohexa-2,5-dienone ligands L^1 and L^2 (adducts **I**, **II**, and **III**) are synthesized. The structures of coordinated complexes **I**, **II**, and **III** are determined by X-ray diffraction (XRD) (CIF files CCDC nos. 1838319 (**II**) and 1838310 (**III**)) and confirmed by the ^{1}H, ^{13}C, and ^{113}Cd NMR spectroscopy (for complexes **I** and **III**) and IR spectroscopy data.

Keywords: redox-active ligands, indophenols, cadmium(II) complexes, tetranuclear cadmium(II) complexes, XRD

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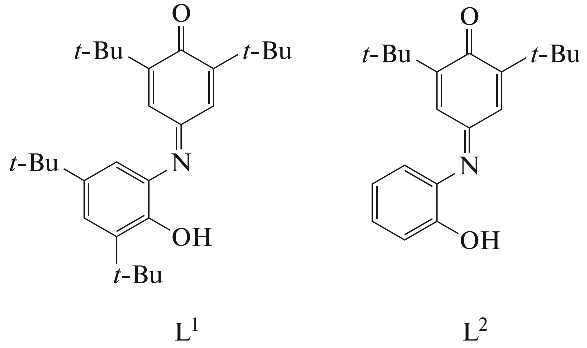
INTRODUCTION

The coordination cadmium compounds were assigned by the World Health Organization to three most toxic types of substances along with the lead and mercury compounds [1]. Increasing interest in studying their structures and properties is caused, to a significant extent, by the recently found high antimicrobial resistance [2, 3] and enhanced activity against cancerous stem cells [4] exhibited by the Cd(II) complexes with organic ligands. The ligands forming complexes of this type are predominantly presented by the polydentate chelating structures based on the hydroxy and thio derivatives of Schiff bases and hydrazones [3–9]. It seems of interest to use the ligands with scattered redox-active sites capable of both coordinating with the metal atom and participating in redox processes in the bound form. In this work, we synthesized and studied the crystal and molecular structures of new hexacoordinated Cd(II) complexes with the redox amphoteric 2,6-di-(*tert*-butyl)-4-((2-hydroxyphenyl)imino)cyclohexa-2,5-dienone ligands (L^1 and L^2) bearing two active redox sites: phenol and *p*-quinoneimine [10, 11] (Scheme 1).



Scheme 1.

EXPERIMENTAL

All reagents and solvents were purchased from commercial providers (Aldrich) and used as received. *o*-Indophenols L^1 and L^2 used in the synthesis were synthesized according to a described procedure [11]. The compounds were characterized by ^{1}H, ^{13}C, and ^{113}Cd NMR spectroscopy. NMR spectra were detected on Varian UNITY-300 (300 MHz for ^{1}H) and Bruker AVANCE-600 (600 MHz for ^{1}H, 151 MHz for ^{13}C, and 133 MHz for ^{113}Cd) spectrometers at the Molecular Spectroscopy Center for Collective Use of the Southern Federal University (Rostov-on-Don) in solutions of $CDCl_3$, DMSO-d_6, and acetone-d_6. Signals were assigned to the signals of residual protons of the deuterated solvents (7.24, 2.49, and 2.05 ppm, respectively, for ^1H) and (77.0 ppm, 39.5, 206.3, and 29.8 ppm for ^{13}C). The ^{113}Cd chemical shifts are presented relative to the reference compound Me_2Cd ($\delta = 0$ ppm). The IR spectra of polycrystalline samples of the studied compounds were recorded on Varian Excalibur 3100 FRT-IR and Bruker Vertex 70 spectrometers. Elemental analyses to C, H, and N were carried out on a Carlo Erba Instruments TCM 480 instrument.

Synthesis of bis(2,6-di-(*tert*-butyl)-4-((2-phenolato)imino)cyclohexa-2,5-dienone)cadmium (I). A solution of Cd(II) acetate dihydrate (0.133 g, 0.5 mmol) in methanol (10 mL) was added to a solution of *o*-indophenol L^1 (0.423 g, 1.0 mmol). The reaction mixture was heated for 30 min and after cooling left to stay at room temperature for 24 h. The precipitate was filtered off and dried. The dark green crystalline powder was obtained. The yield was 68%. $T_m = 224°C$.

IR (ν, cm^{-1}): 2953 (CH_3), 2906 (CH_3), 2866 (CH_3), 1631 (C=O), 1613 ($C=N_{cycle}$), 1477 ($C=C_{ar}$), 1455 ($C=C_{ar}$). ^1H NMR (acetone-d_6; δ, ppm; $^3J_{H-H}$, Hz): 1.05 (s, 18H, $2(CH_3)_3$), 1.21 (s, 18H, $2(CH_3)_3$), 1.29 (s, 18H, $2(CH_3)_3$), 1.45 (s, 18H, $2(CH_3)_3$), 6.78 (s, 2H, H_{ap}), 7.24–7.41 (m, 6H, H_{ar}). ^{13}C NMR (acetone-d_6, δ, ppm): 31.31, 34.21, 35.31, 35.73, 54.07, 68.59, 68.72, 119.28, 124.47, 127.04, 128.50, 130.29, 134.15, 135.26, 136.49, 140.46, 150.66, 151.09, 152.24, 153.58, 165.80, 186.92, 197.48, 209.31, 209.34. ^{113}Cd NMR (acetone-d_6, δ, ppm): –637.98.

For $C_{56}H_{80}N_2O_4Cd$

Anal. calcd., %	C, 70.23	H, 8.42	N, 2.93
Found, %	C, 70.17	H, 8.49	N, 2.98

Synthesis of bis(2,6-di-(*tert*-butyl)-4-((2-phenolato)imino)cyclohexa-2,5-dienone)(2,2'-dipyridyl)cadmium (II). A solution of Cd(II) acetate dihydrate (0.133 g, 0.5 mmol) in methanol (10 mL) was added to a solution of *o*-indophenol L^1 (0.423 g, 1.0 mmol) and 2,2'-dipyridyl (0.078 g, 0.5 mmol) in methanol (30 mL). The reaction mixture was heated for 30 min and after cooling left to stay at room temperature for 24 h. The precipitate was filtered off and dried. The dark green crystalline powder was obtained. The yield was 64%. $T_m = 210°C$.

IR (ν, cm^{-1}): 2951 (CH_3), 2907 (CH_3), 2865 (CH_3), 1653 (C=O), 1607 ($C=N_{cycle}$), 1479 ($C=C_{ar}$), 1454 ($C=C_{ar}$).

For $C_{66}H_{88}N_4O_4Cd$

Anal. calcd., %	C, 71.17	H, 7.96	N, 5.03
Found, %	C, 71.14	H, 7.94	N, 5.04

Synthesis of hexa(2,6-di-(*tert*-butyl)-4-((2-phenolato)imino)cyclohexa-2,5-dienone)bis(acetato)tetracadmium (III). A solution of Cd(II) acetate dihydrate (0.133 g, 0.5 mmol) in methanol (10 mL) was added to a solution of *o*-indophenol L^2 (0.423 g, 1.0 mmol) in methanol (30 mL). The reaction mixture was heated for 30 min and after cooling left to stay at room temperature for 24 h. The precipitate was filtered off and dried. The violet crystalline powder was obtained. The yield was 85%. $T_m = 300°C$.

IR (ν, cm^{-1}): 2999 (CH_3), 2959 (CH_3), 2869 (CH_3), 1686 (C=O), 1624 ($C=N_{cycle}$), 1587 ($C=N_{cycle}$), 1482 ($C=C_{ar}$), 1455 ($C=C_{ar}$). ^1H NMR (DMSO-d_6; δ, ppm; $^3J_{H-H}$, Hz): 0.84 (s, 36H, $4(CH_3)_3$), 1.01 (s, 36H, $4(CH_3)_3$), 1.03 (s, 18H, $2(CH_3)_3$), 1.40 (s, 18H, $2(CH_3)_3$), 2.14 (s, 6H, $2CH_3$), 5.71 (d, 2H, H_{ar}, $^3J = 8.2$), 5.76 (t, 2H, H_{ar}, $^3J = 8.2$), 6.15 (t, 2H, H_{ar}, $^3J = 8.2$), 6.20 (d, 4H, H_{ar}, $^3J = 7.9$), 6.37 (d, 2H, H_{ar}, $^3J = 8.2$), 6.49 (t, 4H, H_{ar}, $^3J = 7.9$), 6.70 (d, 2H, H_{ar}, $^3J = 2.3$), 6.92 (d, 4H, H_{ar}, $^3J = 2.5$), 7.02 (d, 4H, H_{ar}, $^3J = 2.5$), 7.28 (t, 4H, H_{ar}, $^3J = 7.9$), 7.66 (d, 4H, H_{ar}, $^3J = 7.9$), 7.84 (d, 2H, H_{ar}, $^3J = 2.3$). ^{13}C NMR (DMSO-d_6; δ, ppm): 29.13, 29.46, 29.55, 29.85, 35.52, 35.58, 35.87, 116.51, 116.70, 121.69, 122.02, 123.69, 124.73, 125.48, 125.69, 130.80, 131.88, 132.39, 132.96, 135.43, 135.99, 152.09, 153.41, 153.82, 153.94, 157.29, 159.24, 161.79, 180.64, 186.42, 188.12. ^{113}Cd NMR (DMSO-d_6, δ, ppm): –622.53, –691.22.

For $C_{124}H_{150}N_6O_{16}Cd_4$

Anal. calcd., %	C, 61.28	H, 6.22	N, 3.46
Found, %	C, 61.26	H, 6.23	N, 3.47

XRD was carried out on a Bruker APEX II Duo diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). Hydrogen atoms were localized from the difference Fourier electron density syntheses and refined in the isotropic approximation by the riding model. The structures were solved and refined using the SHELXTL PLUS software [12]. The main crystallographic data and structure refinement parameters for compounds **II** and **III** are given in

Table 1. Main crystallographic data and structure refinement parameters for compounds **II** and **III**

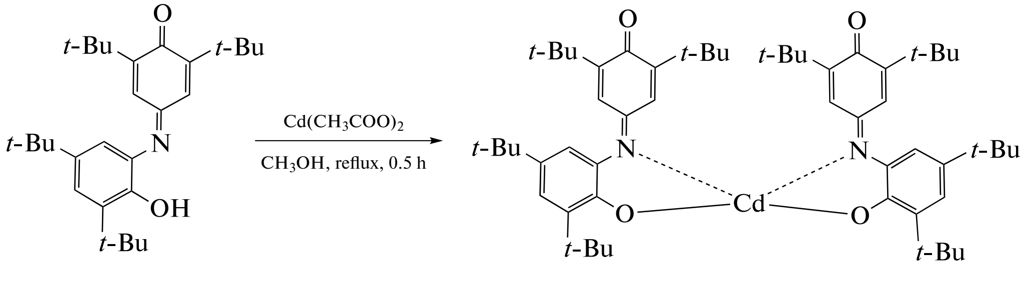
Parameter	Value	
	II	**III**
Empirical formula	$C_{69}H_{100}CdN_4O_7$	$C_{124}H_{150}Cd_4N_6O_{16}$
FW	1209.92	2436.22
T, K	120(2)	120(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	1
a, Å	10.849(2)	12.950(5)
b, Å	27.151(5)	13.724(5)
c, Å	23.083(5)	17.225(6)
α, deg	90	86.269(6)
β, deg	91.74(3)	82.727(6)
γ, deg	90	80.170(5)
V, $Å^3$	6796(2)	2989.1(19)
ρ_{calc}, g cm^{-3}	1.183	1.353
μ, cm^{-1}	0.373	0.766
F(000)	2584	1259
$2\theta_{max}$, deg	50	50
Number of measured reflections	86077	23865
Number of independent reflections	26958	13506
Number of reflections with $I > 2\theta(I)$	19512	7541
Number of refined parameters	785	699
R_1, wR_2 ($I > 2\theta(I)$)	0.0427, 0.0991	0.0543, 0.0999
R_1, wR_2 (all data)	0.0696, 0.1118	0.1198, 0.1238
GOOF	1.014	0.904
$\Delta\rho_{max}/\rho_{min}$, e $Å^{-3}$	0.008/0.000	0.001/0.000

Table 1. Selected bond lengths and bond angles are listed in Table 2.

The full XRD data for compounds **II** and **III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1838319 and 1838310; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of ligand L^1 (in which the *o*-hydroxyl site is sterically hindered by two bulky *tert*-butyl groups) with cadmium acetate affords tetrahedral complex **I** (Scheme 2). The structure of complex **I** was determined by ^1H, ^{13}C, and ^{113}Cd NMR spectroscopy (^{113}Cd NMR, acetone-d_6, δ = –637.98 ppm) and IR spectroscopy.



L^1 **I**

Scheme 2.

Table 2. Selected bond lengths (Å) and bond angles (deg) in complexes **II** and **III**

Bond	*d*, Å	Bond	*d*, Å
II			
Cd(1)–O(1A)	2.2548(12)	O(1A)–C(2A)	1.3157(18)
Cd(1)–(O1)	2.2734(11)	O(2)–C(10)	1.2494(19)
Cd(1)–N(1)	2.3550(14)	O(2A)–C(10A)	1.2499(19)
Cd(1)–N(1A)	2.3610(13)	N(1)–C(1)	1.4036(19)
Cd(1)–N(1B)	2.3650(14)	N(1)–C(7)	1.3188(19)
Cd(1)–N(2B)	2.3757(15)	N(1A)–C(1A)	1.3970(19)
O(1)–C(2)	1.3158(18)	N(1A)–C(7A)	1.3182(19)
III			
Cd(1)–O(1)	2.231(4)	O(1)–C(2)	1.336(6)
Cd(1)–O(1B)	2.253(3)	O(1A)–C(1A)	1.347(7)
Cd(1)–N(1B)	2.331(4)	O(1B)–C(1B)	1.342(6)
Cd(1)–O(1A)	2.341(4)	O(2)–C(10)	1.220(7)
Cd(1)–O(1A)	2.363(3)	O(2A)–C(10A)	1.227(6)
Cd(1)–N(1)	2.391(4)	O(2B)–C(10B)	1.218(6)
Cd(2)–O(1)	2.247(4)	N(1)–C(1)	1.408(7)
Cd(2)–O(1B)	2.275(4)	N(1)–C(7)	1.309(6)
Cd(2)–O(1S)	2.285(4)	N(1A)–C(2A)	1.406(7)
Cd(2)–N(1A)	2.337(5)	N(1A)–C(7A)	1.307(7)
Cd(2)–O(2S)	2.348(4)	N(1B)–C(2B)	1.419(6)
Cd(2)–O(1A)	2.372(4)	N(1B)–C(7B)	1.302(6)
Angle	**ω**, deg	Angle	**ω**, deg
II			
O(1A)Cd(1)O(1)	176.69(4)	N(1)Cd(1)N(1B)	98.21(5)
O(1A)Cd(1)N(1)	105.77(5)	N(1A)Cd(1)N(1B)	162.62(5)
O(1)Cd(1)N(1)	71.15(4)	O(1A)Cd(1)N(2B)	87.33(5)
O(1A)Cd(1)N(1A)	71.71(4)	O(1)Cd(1)N(2B)	95.91(5)
O(1)Cd(1)N(1A)	107.14(4)	N(1)Cd(1)N(2B)	163.84(5)
N(1)Cd(1)N(1A)	96.03(5)	N(1A)Cd(1)N(2B)	97.09(5)
O(1A)Cd(1)N(1B)	94.76(5)	N(1B)Cd(1)N(2B)	70.79(5)
O(1)Cd(1)N(1B)	86.95(5)		
III			
O(1)Cd(1)O(1B)	173.67(14)	O(1)Cd(2)O(1B)	103.83(13)
O(1)Cd(1)N(1B)	112.79(14)	O(1)Cd(2)O(1S)	103.84(14)
O(1B)Cd(1)N(1B)	72.83(14)	O(1B)Cd(2)O(1S)	102.49(15)
O(1)Cd(1)O(1A)	93.01(13)	O(1)Cd(2)N(1A)	143.01(15)
O(1B)Cd(1)O(1A)	81.67(13)	O(1B)Cd(2)N(1A)	85.78(15)
N(1B)Cd(1)O(1A)	153.81(13)	O(1S)Cd(2)N(1A)	108.82(15)
O(1)Cd(1)O(1A)	76.01(12)	O(1)Cd(2)O(2S)	93.22(15)
O(1B)Cd(1)O(1A)	106.15(13)	O(1B)Cd(2)O(2S)	156.51(15)
N(1B)Cd(1)O(1A)	102.11(14)	O(1S)Cd(2)O(2S)	57.07(17)
O(1A)Cd(1)O(1A)	79.02(14)	N(1A)Cd(2)O(2S)	90.25(16)
O(1)Cd(1)N(1)	72.11(14)	O(1)Cd(2)O(1A)	75.52(12)
O(1B)Cd(1)N(1)	104.78(14)	O(1B)Cd(2)O(1A)	80.57(12)
N(1B)Cd(1)N(1)	97.15(15)	O(1S)Cd(2)O(1A)	176.93(15)
O(1A)Cd(1)N(1)	95.00(14)	N(1A)Cd(2)O(1A)	70.93(14)
O(1A)Cd(1)N(1)	147.20(14)	O(2S)Cd(2)O(1A)	119.89(16)

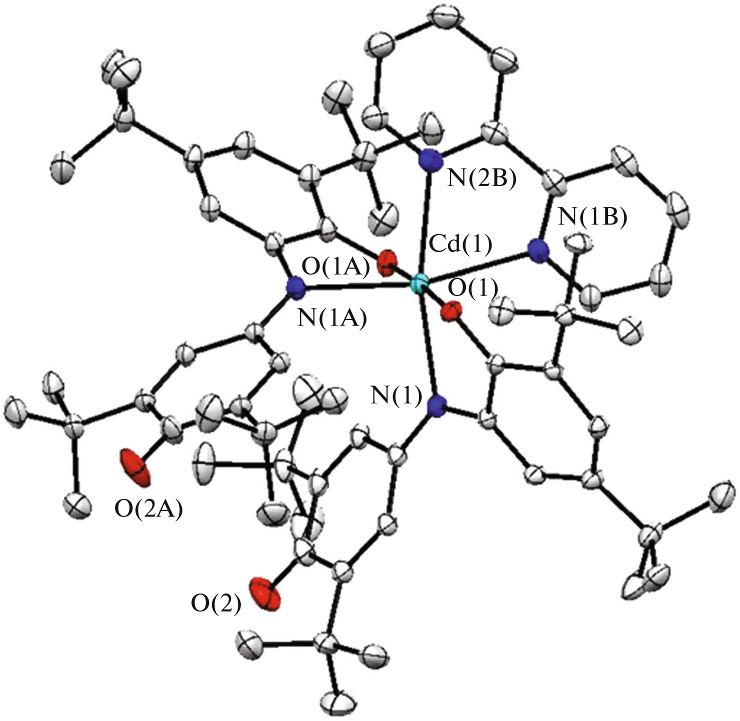
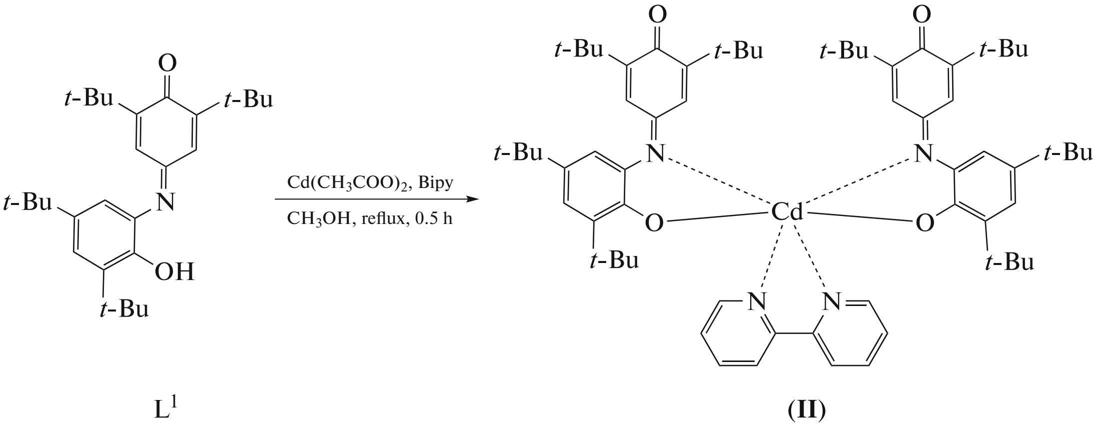


Fig. 1. Molecular structure of complex **II** (hydrogen atoms are omitted, and other atoms are presented by thermal ellipsoids of 50% probability).

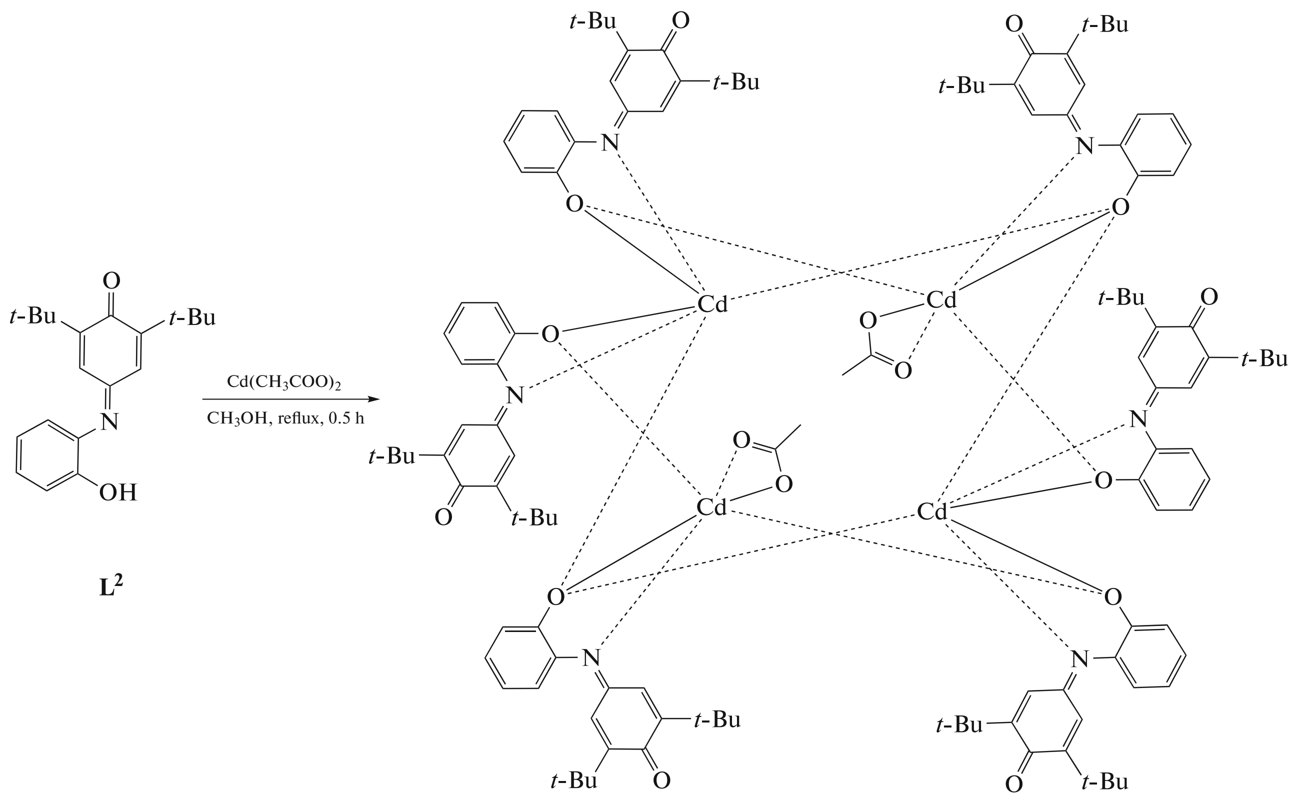
The reaction of ligand L^1 with cadmium acetate in the presence of an equimolar amount of *N*,*N*-chelating 2,2'-dipyridyl affords octahedral complex **II** (Scheme 3) in a yield of 64%. The structure of complex **II** was determined by XRD (Fig. 1) and IR spectroscopy.



Scheme 3.

The XRD study of complex **II** shows that due to 2,2'-dipyridyl the coordination site exists as a distorted octahedron in which the cadmium atom is coordinated to two oxygen atoms (bond lengths 2.2548(12) and 2.2734(11) Å) and four nitrogen atoms (bond lengths 2.3550(14)–2.3757(15) Å). The C(1)N(1)C(7) bond angles in the ligands are 123.76° and 124.30°, respectively. The C–O(1) and C–O(1A) bond lengths in the coordination site (1.3157(18)–1.3158(18) Å) correspond to the catecholate redox form of the ligand [13].

Unlike sterically hindered ligand L^1, its analog with the unhindered hydroxyl group L^2 reacts with cadmium(II) acetate (Scheme 4) to form tetranuclear complex **III** with the unusual molecular structure. The ^{113}Cd NMR spectrum of complex **III** exhibits the signals of the cadmium atoms of two different structural types (Fig. 2).



(III)

Scheme 4.

As follows from the XRD data on the molecular structure of complex **III** (Fig. 3), six molecules of ligand L^2 are coordinated by four cadmium atoms of two types and additionally by two acetate fragments. All four cadmium atoms are located at the centers of the distorted octahedra. The Cd(1) atoms are coordinated by two nitrogen atoms (2.331 and 2.391 Å) and four oxygen atoms of four ligands (2.230–2.362 Å), whereas the Cd(2) atoms are coordinated by one nitrogen atom (2.337 Å) and five oxygen atoms (2.247–2.372 Å) of three ligands and one acetate fragment. Note that the O(1) and O(1B) atoms simultaneously coordinate the Cd(1) atom and Cd(2) atom, whereas the O(1A) atoms simultaneously coordinate two Cd(1) atoms and one Cd(2) atom. The C(2)N(1)C(7) bond angles in the ligands are 121.42°, 121.28°, and 124.09°, respectively. The planes of the phenol and cyclohexadienone cycles of the ligand are turned out relatively to each other by 44.30°, 35.93°, and 40.76°, respectively. The C–O bond lengths of the coordination site (1.336(6)–1.347(7) Å) correspond to the catecholate redox form of the ligand [13].

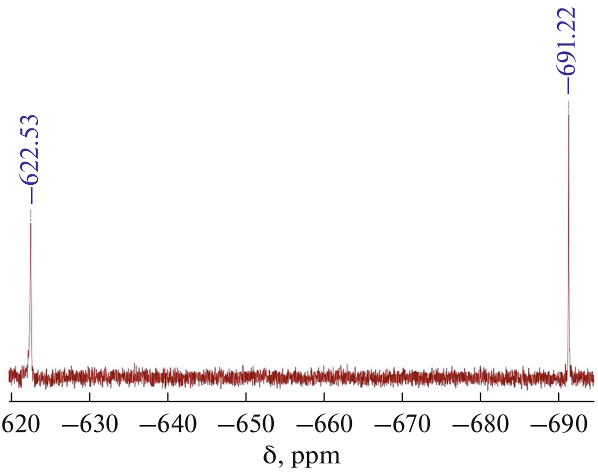


Fig. 2. ^{113}Cd NMR spectrum of complex **III** ($CDCl_3$, 303 K).

The carboxylate cadmium(II) complexes that form cubic polynuclear structures with four cadmium atoms and bridging oxygen atoms have previously been described [14–16]. However, in the case of complex **III**, the formation of the cubic structure is hindered

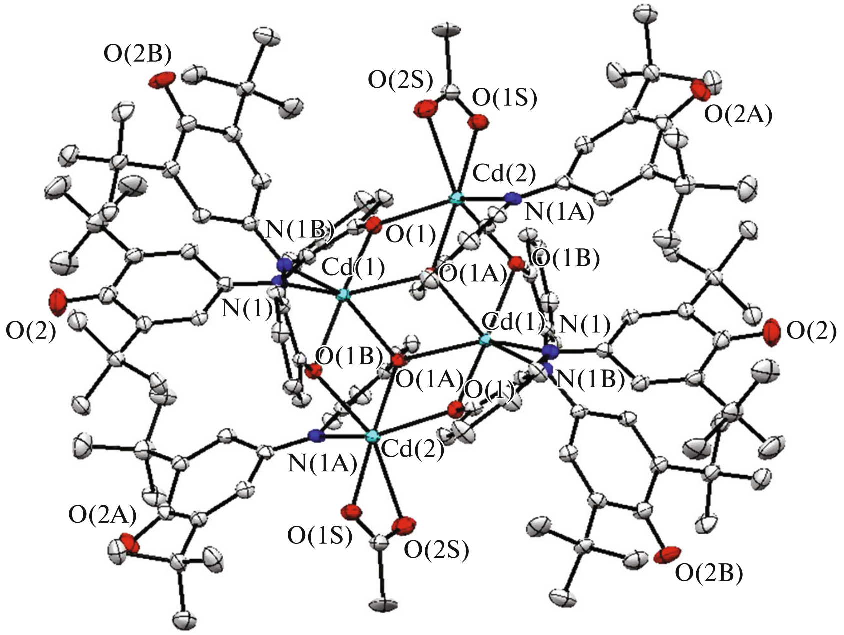


Fig. 3. Molecular structure of complex **III** (hydrogen atoms are omitted, and other atoms are presented by thermal ellipsoids of 50% probability).

probably due to the steric effect of the indophenol ligands with the bulky *tert*-butyl ligands. The "external" Cd(2) atoms remain to be coordinated by the acetate groups [17].

Thus, the reaction of *o*-indophenol ligands L^1 and L^2 with cadmium(II) acetate affords complexes of various compositions. Using ligand L^1 with two sterically hindered bulky *tert*-butyl groups in the indophenol fragment as an example, the formation of the complex with the tetrahedral coordination site and a possibility of its additional coordination by the *N*,*N*-chelating compounds to the complex with the octahedral coordination site were shown. The absence of bulky *tert*-butyl groups in the indophenol fragment of ligand L^2 eliminates steric restraints to form the polynuclear Cd(II) complexes.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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