Polyhedron 110 (2016) 235–240

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterizations of new cadmium complexes based on poly(aza)arene-annelated 2,2′-bipyridines

Dmitry S. Kopchuk [a,b,*], Pavel A. Slepukhin [a,b], Igor S. Kovalev [a], Albert F. Khasanov [a], Olga S. Taniya [a], Olga V. Shabunina [a], Grigory V. Zyryanov [a,b], Vladimir L. Rusinov [a,b], Oleg N. Chupakhin [a,b]

[a] Ural Federal University, 19, Mira St., 620002 Yekaterinburg, Russian Federation
[b] Postovsky Institute of Organic Synthesis of RAS (Ural Division), 22/20, S. Kovalevskoy/Akademicheskaya St., 620990 Yekaterinburg, Russian Federation

ARTICLE INFO

Article history:
Received 4 December 2015
Accepted 28 February 2016
Available online 4 March 2016

Keywords:
Cd(II) complex
Poly(aza)arenes
2,2′-Bipyridines
Polyaromatic ligands
Crystal structure

ABSTRACT

We have developed an efficient synthesis of new cadmium(II)-containing complexes based on poly(aza) arene-annelated 2,2′-bipyridines. All the complexes were characterized by X-ray structural analysis. The influence of the type of the ligand at the structural properties of the complexes has been studied.

1. Introduction

Nowadays, the chemistry of coordination compounds of cadmium attracts special attention due to their high biotoxicity and related environmental issues [1–4]. In addition, the complexing properties of Cd(II) are heavily utilized for the construction of coordination polymers [5] and supramolecular structures studies [6]. Very recently photophysical properties of 1,1′-binaphthalenyl-2,2′-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid-based Cd(II) and Zn(II) complexes have been studied [7].

According to the Cambridge Structural Database about 150 structures of cadmium complexes formed around the central ion by the coordination of two 2,2′-bipyridine type ligands [8]. In the majority of cases the ligands are 2,2′-bipyridine derivatives, only very few structures are based on phenanthroline ligands, while complexes of other azaheterocycles in the database are not represented. Moreover, poly(aza)arene-annelated analogs of 2,2′-bipyridine type ligands, as well as their metal chelates, have been described by only a few examples in a literature [9].

In the current work to investigate the influence of polyaromatic ligands on the geometry of the coordination node we have studied a number of Cd(II) complexes with polyannelated analogs of 2,2′-bipyridine type ligands. For this purpose several 2,2′-bipyridine-type ligand have been used, which differ in the number and arrangement of phenyl substituents in the anneleted pyridine rings: in one case there is rigid fixation of aromatic rings (azatriphenylene-type ligand), while in the other cases the phenyl substituents may rotate freely.

2. Experimental

XRD experiments were performed on an automated single crystal diffractometer «Xcalibur 3» by standard procedures (graphite monochromated Mo Kα radiation, $T = 295\ (2)$ K, ω-scans with step 1°).

For the analysis of complex **1** the chip of yellow crystal with a geometric size of 0.24 × 0.16 × 0.08 mm has been used. For the analysis of complex **2** a piece of colorless plate size of 0.14 × 0.08 × 0.02 mm has been used. For the analysis of complex **3** a chip of yellow prism size of 0.16 × 0.11 × 0.07 mm has been used. The analytical absorption correction by the model multifaceted crystal has been introduced [10]. Solution and refinement of the structure carried out using the software package SHELX [11]. The structure was solved by direct methods and refined by full-matrix of F^2 in an anisotropic approximation for non-hydrogen atoms. Hydrogen atoms are added to the calculated positions and included in the refinement model “rider” in the isotropic approximation with dependent thermal parameters. For the analysis of complex **3** the empirical absorption correction was applied [12]. The general crystallographic parameters and results of the structures refinement are presented in the Table 1.

---

[*] Corresponding author at: Ural Federal University, 19, Mira St., 620002 Yekaterinburg, Russian Federation. Tel.: +7 343 375 4501; fax: +7 343 374 0458.
E-mail address: dkopchuk@mail.ru (D.S. Kopchuk).

http://dx.doi.org/10.1016/j.poly.2016.02.047
0277-5387/

Table 1
Selected bond lengths for cadmium complexes **1–3**.

1		2		3	
Bond	Å	Bond	Å	Bond	Å
Cd1 N1	2.277(5)	Cd1 N2	2.287(6)	Cd1 N1	2.318(6)
Cd1 N2	2.427(5)	Cd1 N1	2.491(5)	Cd1 N3	2.321(6)
Cd1 N3	2.358(6)	Cd1 I2	3.0585(7)	Cd1 N2	2.481(6)
Cd2 I1	2.8581(8)	Cd2 I2	2.8486(7)	Cd1 N4	2.484(6)
Cd2 I2	2.7195(8)	I1 Cd2	2.7372(8)	Cd1 I1	2.9831(11)
Cd2 I3	2.7004(8)			Cd1 I2	2.9837(10)
				I1 Cd2	2.774(4)
				Cd2 I3	2.763(5)
				Cd2 I4	2.619(9)

2.1. General procedure for the preparation of isoquinolines *4,6*

Mixture of corresponding 5,6,7,8-tetrahydroisoquinoline [13] (0.5 mmol), DDQ (114 mg, 0.5 mmol) and *o*-xylene (40 ml) was refluxed for 3 h. Second portion of DDQ (114 mg, 0.5 mmol) was added and the resulting mixture was refluxed for 3 h. Then third portion of DDQ (114 mg, 0.5 mmol) was added and the resulting mixture was refluxed for 4 h. Solvent was removed under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, chloroform).

2.1.1. 3-Phenyl-1-(2-pyridyl)isoquinoline *4*

Yield 51%. $C_{20}H_{14}N_2$. M.p. 107–109 °C. NMR ^1H ($CDCl_3$, δ, ppm): 7.43 (m, 3H, Ph), 7.52 (m, 2H, isoquin.), 7.58 (м, 1H, isoquin.), 7.69 (m, 1H, isoquin.), 7.94 (m, 2H, Ph), 8.15 (s, 1H, H-4), 8.22 (m, 2H, py), 8.75 (d, 1H, ^3J = 8.4 Hz, py), 8.81 (d, 1H, ^3J = 4.8 Hz, H-6' (Py)). NMR ^{13}C ($CDCl_3$, δ, ppm): 117.0, 123.2, 125.6, 127.0, 127.4, 127.5, 128.0, 128.5, 128.6, 128.8, 130.1, 137.0, 138.2, 139.5, 148.3, 149.8, 157.0, 158.8. ESI-MS, *m*/*z*: found 283.12, required 283.12 $(M+H)^+$. Elemental analysis (calcd): C 85.08, H 5.00, N 9.92. Found, %: C 84.81, H 4.80, N 9.61.

2.1.2. Complex *1*

A crystal sample of cadmium complex **1** suitable for X-ray structural analysis was obtained by slow evaporation of solution of ligand (20 mg) and CdI_2 (26 mg, 1 eq.) in acetonitrile (5 ml). Off-white crystals. $C_{44}H_{34}Cd_3I_6N_6$. Elemental analysis (calcd): C, 30.28; H, 1.96; N, 4.81. Found, %: C 30.21, H 2.07, N 5.01. CCDC 1438668 contains the supplementary crystallographic data for this complex.

2.2. Synthesis of 10-(pyridin-2-yl)-12,13-dihydro-11H-dibenzo[f,h]cyclopenta[c]quinoline 5 (monoazatriphenylene) *5*

A mixture of triazatriphenylene [14] (0.4 g, 1.3 mmol) and the 1-morpholinocyclopentene (1.04 ml, 6.49 mmol) was stirred under an argon atmosphere at 200 °C for 2 h. An additional portion of the 1-morpholinocyclopentene (0.52 ml, 3.25 mmol) was added, and the mixture was stirred at 200 °C for a further 1 h. The reaction mixture was cooled to room temperature, acetonitrile (30 ml) was added, and stirring continued for 3 h. The precipitate formed was filtered off, washed with acetonitrile, and dried. Yield 0.35 g (1.01 mmol, 78%). $C_{25}H_{18}N_2$. M.p. 181–183 °C. NMR ^1H ($CDCl_3$, δ, ppm): 2.25 (2H, m, CH_2), 3.63 (2H, t, ^3J = 7.2 Hz, CH_2), 3.73 (2H, t, ^3J = 7.2 Hz, CH_2), 7.33 (1H, m, H-5′(Py)), 7.62–7.74 (4H, m, $CH_{arom.}$), 7.92 (1H, ddd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, H-4′(Py)), 8.60 (1H, m, H-3′ (Py)), 8.63–8.77 (4H, m, H-6’(Py)+ $CH_{arom.}$), 9.51 (1H, m, H-8). NMR ^{13}C ($CDCl_3$, δ, ppm): 26.1, 33.2, 37.4, 122.4, 122.9, 123.1, 123.3, 123.7, 126.1, 126.6, 127.2, 127.3, 127.7, 128.3, 130.1, 130.8, 131.1, 131.8, 136.4, 138.9, 144.9, 148.5, 150.3, 151.9, 158.9. ESI-MS, *m*/*z*: found 347.15, calculated 347.15 $(M+H)^+$. Elemental analysis (calcd): C 86.68; H 5.24; N 8.09. Found: C, 86.52; H, 5.11; N, 7.88 (see Tables 2 and 3).

2.2.1. Complex *2*

A crystal sample of cadmium complex **3** suitable for X-ray structural analysis was obtained by slow evaporation of solution of ligand (20 mg) and CdI_2 (21 mg, 1 eq.) in acetonitrile (5 ml). Off-white crystals. $C_{52}H_{36}Cd_2I_4N_4$. Elemental analysis (calcd): C, 43.09; H, 2.50; N, 3.87. Found: C, 42.99; H, 2.69; N, 3.77. CCDC 1438670 contains the supplementary crystallographic data for this complex.

2.2.2. 3,4-Diphenyl-1-(2-pyridyl)isoquinoline *6*

Yield 68%. $C_{26}H_{18}N_2$. M.p. 182–184 °C. NMR ^1H ($CDCl_3$, δ, ppm): 7.07–7.24 (m, 3H), 7.26–7.34 (m, 2H), 7.35–7.51 (m, 6H), 7.59 (m, 2H), 7.71 (m, 1H), 7.91 (ddd, 1H, ^3J 7.8, 7.8 Hz, ^4J 1.8 Hz, H-4′), 8.16 (d, 1H, ^3J 7.8 Hz), 8.72 (m, 1H), 8.81 (dd, 1H, ^3J 4.8 Hz, ^4J 1.6 Hz, H-6′). NMR ^{13}C ($CDCl_3$, δ, ppm): 123.2, 125.4, 125.6, 126.0, 127.1, 127.4, 127.5, 127.6, 127.7, 128.3, 130.1, 130.5, 131.1, 131.3, 137.0, 137.3, 137.5, 140.9, 148.5, 149.4, 156.7, 158.7. ESI-MS, *m*/*z*: found 359.15, calculated 359.15 $(M+H)^+$. Elemental analysis (calcd): C 87.12, H 5.06, N 7.82. Found, %: C 86.92, H 4.88, N 7.51.

2.2.3. Complex *3*

A crystal sample of cadmium complex **2** suitable for X-ray structural analysis was obtained by slow evaporation of solution of ligand (20 mg) and CdI_2 (26 mg, 1 eq.) in acetonitrile (5 ml). Off-white crystals. $C_{50}H_{36}Cd_2I_4N_4$. Elemental analysis (calcd): C, 42.13; H, 2.55; N, 3.93. Found: C, 42.21; H, 2.33; N, 3.78. CCDC 1438669 contains the supplementary crystallographic data for this complex.

3. Results and discussions

The ligands used for the preparation of cadmium complexes were synthesized according to the previously reported [13,14] “1,2,4-triazine” methodology (Scheme 1). Thus, the aza-Diels–Alder reaction between 1,2,4-triazines and 1-morpholinocycloalkenes allows to obtain corresponding cycloalkene-annelated 2,2′-bipyridine ligands. For the synthesis of ligands **4** and **6** the aromatization of cyclohexane cycle was carried out by means of DDQ, and cyclopentane-anneleted ligand **5** has been used as is.

Looking at the structures of the ligands **4–6** one can suggest that the main differences between these ligands implies the phenyl ring in position 3 in the isoquinoline ring or, in case of ligand **5**, in an alpha-position with reference to a nitrogen atom: in ligand **4** this phenyl ring is free to rotate; in ligand **5** the phenyl ring is fused to the one in position 4; and in ligand **6** it may show a preferred disposition due to the presence of the phenyl ring in position 4.

One can suggest that these structural features of the herein reported ligands would affect their chelating properties toward metal cations, for instance Zn(II) or Cd(II) cations, as well as the geometry of the coordination node.

To confirm our suggestion, at the next step Cd(II) complexes **1–3** of poly(aza)annelated analogs of 2,2′-bipyridine ligands **4–6** were prepared according to reported procedures (See Section 2).

According to X-ray data, compound **1** with the $[Cd(Het)_2(C_2H_3N)_2]^{2+}[Cd_2I_6]^{2-}$ composition crystallizes in the centrosymmetric system space group *C2/c* (Fig. 1). The chelated cation is located in a special position with cadmium atom on the axis of order 2 (Fig. 1). The ball-and-stick model was selected for the graphical representation of the structure of complex **1**, because of the strong overlapping in case of the atomic thermal ellipsoids plot structure viewing. In this ball-and-stick model the hydrogen atoms are omitted for the simplicity of perception.

Table 2
Selected bond angles (deg.) for complexes **1–3**.

1		**2**		**3**	
Angle	Deg.	Angle	Deg.	Angle	Deg.
N1 Cd1 N1	176.1(2)	N2 Cd1 N2	174.6(3)	N1 Cd1 N3	175.7(3)
N3 Cd1 N2	162.16(18)	N1 Cd1 I2	163.80(12)	N2 Cd1 I1	163.68(15)
N1 Cd1 N3	90.56(19)	N2 Cd1 I2	95.37(16)	N3 Cd1 I1	93.07(19)
N2 Cd1 N2	84.0(2)	N1 Cd1 N1	81.9(2)	N2 Cd1 N4	83.33(19)
N1 Cd1 N2	71.65(17)	N2 Cd1 N1	71.2(2)	N3 Cd1 N2	71.4(2)
C1 N1 Cd1	124.7(4)	C25 N2 Cd1	121.2(6)	C15 N1 C19	119.5(7)
C5 N1 Cd1	116.6(4)	C21 N2 Cd1	117.5(5)	N1 Cd1 N2	105.4(2)
I3 Cd2 I2	123.60(3)	I1 Cd2 I1	123.72(5)	I4 Cd2 I2	125.1(5)
I3 Cd2 I1	110.28(3)	I1 Cd2 I2	112.173(19)	I1 Cd2 I2	92.86(10)
I2 Cd2 I1	104.49(2)	I1 Cd2 I2	103.29(2)	I3 Cd2 I1	106.95(15)
Cd2 I1 Cd2	80.84(2)	Cd2 I2 Cd1	84.63(2)	Cd2 I2 Cd1	87.99(8)
N1C5C6N2	38.8(5)	N2C20C21N2	37.7(5)	N1C2C27N2	37.4(5)
N2C14C15C20	28.7(5)	N1C1C2C3	10.3(5)	N1C10C11C16	45.7(5)

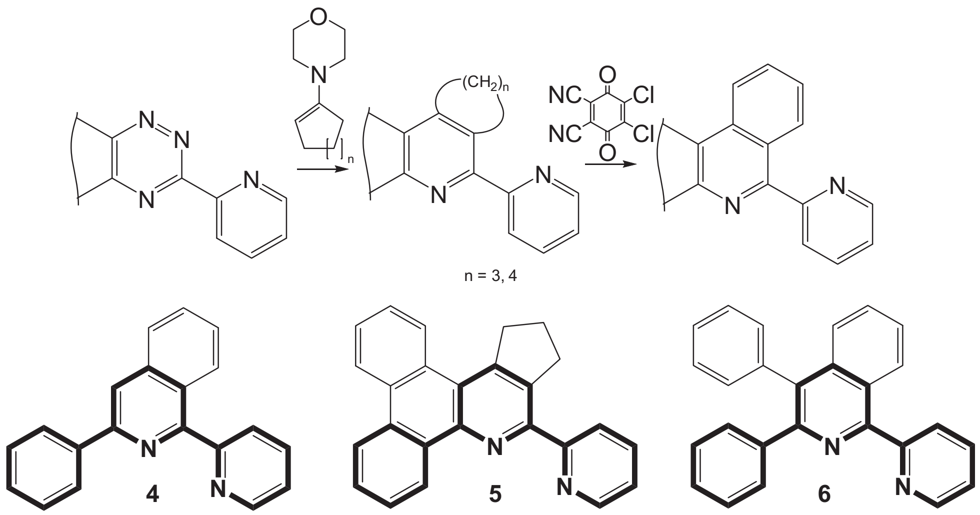
Table 3
Crystal data and structure refinement for complexes **1–3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{44}H_{34}Cd_3I_6N_6$	$C_{50}H_{36}Cd_2I_4N_4$	$C_{52}H_{36}Cd_2I_4N_4$
Formula weight	1745.37	1425.23	1449.25
T (K)	295(2)	295(2)	295(2)
Crystal system	monoclinic	tetragonal	triclinic
Space group	C2/c	$I4_1/a$	$P\bar{1}$
a (Å)	16.9821(15)	14.7635(6)	11.648(2)
b (Å)	14.8490(5)	14.7635(6)	11.695(2)
c (Å)	21.2960(14)	44.2357(7)	20.660(2)
α (°)	90	90	104.485(14)
β (°)	103.964(7)	90	104.615(14)
γ (°)	90	90	95.9740(10)
V (Å^3)	5211.5(6)	9641.7(6)	2594.4(7)
Z	4	8	2
ρ_{calc} (mg/mm^3)	2.225	1.964	1.855
μ (mm^{-1})	4.802	3.481	3.236
Crystal size (mm)	0.24 × 0.16 × 0.08	0.14 × 0.08 × 0.02	0.16 × 0.11 × 0.07
Θ range for data collection	$2.74 < \Theta < 28.29^{\circ}$	$2.68 < \Theta < 26.38^{\circ}$	$2.82 < \Theta < 28.28^{\circ}$
Reflections collected	11419	21999	22509
Independent reflections	6262(R_{int} = 0.0257)	4936(R_{int} = 0.0589)	11665(R_{int} = 0.0527)
Reflections with $I > 2\sigma(I)$	2880	2593	4304
Goodness-of-fit (GOF) on F^2	1.001	1.005	1.026
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0407 wR_2 = 0.1054	R_1 = 0.0444 wR_2 = 0.1149	R_1 = 0.0681 wR_2 = 0.1508
Final R indexes [all data]	R_1 = 0.1010 wR_2 = 0.1120	R_1 = 0.0949 wR_2 = 0.1246	R_1 = 0.1751 wR_2 = 0.1701
Largest difference in peak and hole (e Å^{-3})	1.727/−1.807	2.323/−0.551	1.222/−0.906

The coordination sphere of cadmium is octahedrally distorted. The nearest coordination environment of the metal cation consists of six nitrogen atoms, four of which belong to the 2,2′-bipyridine-type ligands, while the other two belong to nitrogen atoms of acetonitrile molecules. In the non-planar chelate ring a pyridyl moiety is rotated by an angle of 41° with respect to the plane of isoquinoline ring, and cadmium atom is out of the plane of pyridyl cycle by 0.57 Å, and out of the plane of isoquinoline cycle by 1.45 Å. In turn, this leads to serious distortion of the Cd–N bond lengths, which are 2.277 (5), 2.427 (5), 2.358 (6) Å for the pyridyl, isoquinoline and nitrile nitrogens respectively. The bond angles in the N–Cd–N coordination polyhedra are vary from 71.65° (17) to 105.31° (17), and from 176.1° (2) to 162.16° (18) onto the opposite vertices of an octahedron. It is obvious, that the increasing of the length and the weakening of the strength of the bond between Cd(II) atom and the isoquinoline fragment in the complex are connected with the violation of overlapping between unshared nitrogen atoms of ligands and atomic orbital of Cd due to the cadmium atom being out of the plane of heterocyclic ring under the influence of unfavorable steric factors. The conjugation between pyridyl and isoquinolinyl moieties of the ligand is also violated. This is demonstrated by the values of twist angels of 38.8(5)° between pyridine and isoquinoline cycles and the longer than 1.5 Å C–C bond length between these two heterocycles. Such value is more typical for single C–C bonds of non-conjugated systems. For the implementation of π–π interactions the isoquinoline cycles are oriented in the most favorable configuration. The planes of isoquinoline cycles are arranged at an angle of 12° which is nearly coplanar, but the minimum distance between the nearest carbon atoms is greater than 3.5 Å, which does not allow assuming the significant π–π overlapping for these systems. In addition there is a twist between the isoquinoline ring and the phenyl ring in position 3 with the twist angle value of 28.7(5)°. No shortened intermolecular contacts in the crystal structure of the compound **1** have been found.

Anion binuclear complex $[Cd_2I_6]^{2-}$ with two bridging iodine atoms is located in a special position in the center of inversion. The geometry of the anion is standard: in the tetrahedral environment of cadmium atoms Cd–I bond lengths for the bridgehead atoms are similar in size and about 0.1 Å longer than the bond lengths for the terminal iodine atoms (2.8830 (8), 2.8581(8), 2.7195(8), 2.7004 (8) Å, respectively). The I–Cd–I bond angles are ranged from 99.16(2)° to 123.60 (3)°.

Thus, in complex **1** the metal–ligand interaction may be limited to the consideration of the interaction of the chelated metal cation



Scheme 1. The synthesis and structures of polyareneanneleted analogs of 2,2′-bipyridine type ligands **4–6**.

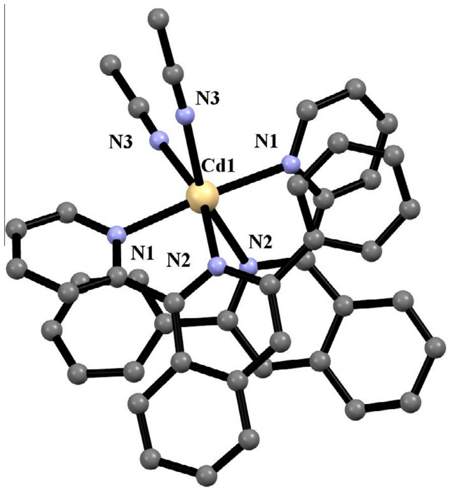


Fig. 1. The ball-and-stick model for the complex **1** (the symmetry operations −*x*, *y*, 0.5−*z* (for the cationic part) and 0.5−*x*, 1.5−*y*, 1−*z* (for the anionic part)). Hydrogen atoms are omitted for clarity.

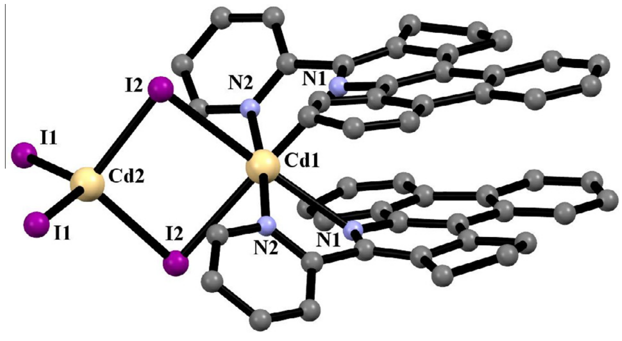


Fig. 2. The ball-and-stick model for the complex **2** (the symmetry operations 1−*x*, 0.5−*y*, *z*). Hydrogen atoms are omitted for clarity.

with different parts of the ligand, while excluding the contributions of intra- and inter-molecular overlap of π-systems in this interaction.

According to the X-ray data, binuclear complex **2** with the $[Cd_2I_4(Het)_2]^{2-}$ composition crystallizes in the centrosymmetric system space group $I4_1/a$. The molecule is located in a special position on the 2-fold rotation axis, extending through the cadmium atoms (Fig. 2), each of those is connected with two bridging iodine atoms. First cadmium atom has a distorted octahedral configuration with four nitrogen atoms and two iodine atoms in the nearest coordination sphere. The increase in Cd–I bond length to 3.0585 (7) Å compared with the standard value of 2.8 Å for the bridgehead Cd–I is apparently due to the influence of bulky heterocyclic ligands. The chelate ring formed by 2,2′-dipyridyl ligands is non-planar with the pyridyl fragment twisted at an angle of 41° to the plane of azatriphenylene cycle. Cadmium atoms are out of the plane of the pyridyl cycle by 0.65 Å, and from the plane of the azatriphenylenyl cycle by 1.50 Å. The Cd–N bond lengths comprise 2.287(6) and 2.491(5) Å for nitrogen atoms for pyridine and azatriphenylene cycle respectively. The values of twist angels of between pyridine and isoquinoline cycle and the isoquinoline ring and the phenyl ring in position 3 are of 10.3(6)° and 37.7(5)° respectively. The values of valence angles of coordination polyhedras are vary from 71.2(2)° to 113.15(19)°, and from 174.6(3)° to 163.80 (12)° on to the opposite vertices of an octahedron. It worth to mention, that this geometry of the chelate ring is almost identical to the geometry observed for the complex **1**.

The coordination sphere of the second cadmium atom is tetrahedrally distorted. The nearest coordination environment of the metal cation is composed by four iodine atoms with Cd–I bond lengths of 2.7372(8) and 2.8486(7) Å for the terminal and bridging atoms, respectively. This is in a good agreement with the standard values. The I–Cd–I bond angles lie in the range from 99.85(2)° (for the angle between two bridging iodine atoms) to 123.72(3)° (for the angle between the end atoms). Thus, the cadmium coordination polyhedron has a geometry which is almost identical to the geometry of the well-studied binuclear anions $Cd_2I_6^{2-}$.

The conclusions about the possibilities of interaction between π-ligand systems in complex **1** are fully transferable to the complex **2**. Despite the somewhat higher coplanarity of two azatriphenylene fragments compared to the isoquinoline ones (the interplanar angle value is 7.5°) and a decrease of the minimum distance between atoms of one heterocycle to the plane of another to 3.43 Å, the observed geometry does not allow concluding that in complex **2** the substantial overlapping of π-systems of ligands takes place.

In that case, complex **2** can be considered as a result of the direct substitution of two acetonitrile molecules in the cationic complexes of type **1** under the action of CdI_4^{2-} anion. After this substitution all basic structural features inherent in the complex **1** are maintained to be the same for the complex **2**. The newly formed Cd–I bridging bonds have an increased length, and evidently less strong compared with similar Cd–I bonds in bridged $Cd_2I_6^{2-}$ anions and similar ones.

The neutral binuclear complex **3** with the [$Cd_2I_4(Het)_2$] composition crystallizes in the centrosymmetric space group $P\bar{1}$. The resolving of the structure may be held in the space group monoclinic system C2/c with unit cell parameters of a = 17.344(4) Å, b = 15.6236(4) Å, c = 21.002(4) Å, β = 114.243(5) of the special position on the axis of the molecule. However, this symmetry is overstated, since it leads to the superposition of the elements of the structure to each other and to the occurrence of abnormal values of bond lengths and bond angles for this complex. Solution in the lower symmetry group, namely *Cc*, permits to solve this problem but results in the generation of the non-positive anisotropic displacement parameters in the process of the structure refinement. Therefore, the structure of the complex has been resolved in the triclinic system with unit cell parameters of a = 11.648(2) Å, b = 11.695(2) Å, c = 20.660(2) Å, α = 104.485(14)°, β = 104.615 (14)°, γ = 95.9740(10)° (matrix transformation 0.5 0.5 0 -0.5 0.5 0 0.5 -0.5 1) in order to allow the considering the elements, regardless of the structure. In general, the geometry of complex **3** matches the geometry of complex **2**. In a rough approach the molecule of complex **3** is rotationally symmetrical, but this symmetry is broken by the presence of a structural disorder due to the presence of terminal iodine atoms (Fig. 3).

The disordered atomic positions of CdI_2 terminal groups are a distinctive feature of this complex. The character of highly anisotropic thermal ellipsoids of terminal iodine atoms, which form the extended zone of high electron density, eliminates the assumption of a superposition of two structures and indicates strong libration at/above the plane of bridging Cd–I bonds. These librations are taken into account by the introduction of the value of disorder for the each iodine atom in the position 3 with the occupancy coefficients of 0.25/0.25/0.50, and by the introduction of value of partially permitted disorder of cadmium atom in the position 2 with the population coefficient of 0.5. In all likelihood, such a structural model is not sufficient for the satisfactory description of the actual distribution of the electron density of terminal iodine atoms in a crystal, as indicated by the high value of divergence (R_1 = 0.0681). But the further increase of the number of components of the disorder is not appropriate in a view of the following rise of the overlapping of ellipsoids, and the increase in uncertainty of their values and atomic coordinates. Noteworthy is that the atoms of the phenyl substituents of adjacent molecules, which are close to the CdI_2 end-group are also exhibit the strong anisotropy of atomic thermal ellipsoids. This can be a good indication of the dependence of the electron density distribution between these groups and CdI_2 terminal groups.

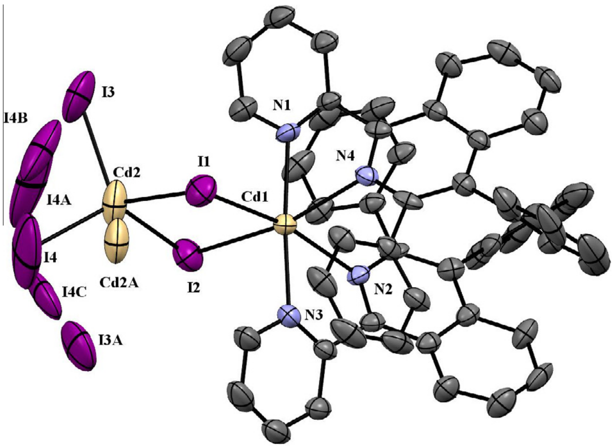


Fig. 3. Crystal structure of the complex **3** according to the X-ray data in the thermal ellipsoids with 30% probability level. Hydrogen atoms are omitted for clarity.

The cadmium atom coordinated to heterocyclic ligands has a distorted octahedral configuration with four nitrogen atoms and two iodine atoms in the nearest coordination sphere. The increase in Cd–I bond length to 3.0585(7) Å compared with the standard value of 2.8 Å for the bridgehead Cd–I, is again due to the influence of bulky heterocyclic ligands. Chelate ring formed by 2,2′-bipyridine ligands is non-planar, the measured values of rotation angles for the pyridyl fragments to the plane of isoquinoline are of 37.4 (5)° and 38.9(6)°. The cadmium atoms are pointed out of the plane of pyridyl cycles by 0.77 and 0.76 Å, and out of the plane of isoquinoline cycles – by 1.31 and 1.35 Å. The Cd–N bond length comprise 2.320(7) and 2.318(7) Å for pyridine and 2.484(7) and 2.481 (7) Å for isoquinoline nitrogens respectively.

The values obtained for the geometric characteristics of the coordination polyhedron of the complex **3** and the above-mentioned complexes **1–2** are somewhat different from the parameters reported for the Cd (II) 2,2′-bipyridine complexes [15a-b] including α-phenyl [15c] or α-methyl-substituted [15d]. For instance, in complexes **1–3** the Cd–N distances for pyridine-type nitrogens are from 2.277(5) Å in complex **1** to 2.320(7) Å in complex **3**, which are typical Cd–N bond lengths for Cd(II) 2,2′-bipyridiene complexes [15]. For nitrogen atoms of isoquinoline or azatryphenylene rings the Cd–N bonds are longer (i.e. weaker) than a typical Cd–N bond length: the Cd–N distances are from 2.427(5) Å in complex **1** to 2.491(5) Å in complex **2** and 2.481(7) in complex **3**. In addition the conjugation between pyridyl and isoquinolinyl or monoazatriphenylenyl moieties of the ligand in the Cd(II) coordination node is violated: the twist angle values are 38.8(5)° in complex **1**, 37.7 (6)° in complex **2**, and 37.4(5)° or 38.9(6)° in complex **3**, which is different from the twist angle values reported for Cd(II) 2,2′-bipyridine complexes [14], typically from 0.5° to 22° [15,16]. These differences in the values of geometric characteristics for complexes **1–3** can be explained first of all by the steric repulsion between the benzene- or cyclopentane-anneleted pyridine moieties and the non-anneleted pyridine ring in the Cd(II) complexes **1–3**. In addition, in complex **3** the influence of the C3-phenyl substituent in the quinolinic core of the ligand must be taken into the account: due to the presence of another phenyl ring in position 4 and the possible Van-der-Waals interaction with the rigidly-fixed pyridine ring of an adjacent ligand molecule of the complex **3** the free rotation of the phenyl substituent at the position C3 is very limited. The interaction between the terminal iodine atoms and phenyl substituents of adjacent molecules results in their spatial disordering. In case of CdI_2-moiety this is manifested in the form of abnormal quantities of anisotropic thermal parameters of iodine atoms, and in case of the phenyl substituent this disordering results in the appearing of highly anisotropic thermal ellipsoids showing the atom librations in the plane of the phenyl ring

4. Conclusion

In summary, an efficient synthesis of new cadmium(II)-containing complexes based on poly(aza)arene-annelated 2,2′-bipyridines has been developed. These complexes were well characterized by X-ray structural analysis. Based on the data collected it was demonstrated that depending on the type of ligand the structural properties of Cd(II) complexes are different from those obtained earlier for 2,2′-bipyridine-type complexes. Thus, the introduction of bulky heterocyclic ligand into the complex resulted in the length increasing, as a result, weakening of Cd–N bonds in all the complexes, and Cd–I bonds in complexes **2–3**. The conjugation between pyridyl and isoquinolinyl or monoazatriphenylenyl moieties of the ligand in the Cd(II) coordination node in complexes **1–3** is also violated. In addition C–C bond lengths between pyridine and isoquinoline fragments for the complex **1** are longer than that of conjugated systems due to the influence of bulky isoquinoline fragment. The studies of the influence of the type of ligand on the photophysical properties of Cd(II) complexes are in progress in our laboratory.

Acknowledgment

This work was supported by Russian Scientific Foundation (Ref. # 15-13-10033).

References

[1] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu, Int. J. Phys. Sci. 2 (5) (2007) 112.
[2] R. Verma1, P. Dwivedi, Recent Res. Sci. Technol. 5 (5) (2013) 98.
[3] F.I. Pinot, S.E. Kreps, M. Bachelet, P. Hainaut, M. Bakonyi, B.S. Polla, Rev. Environ. Health 15 (3) (2000) 299.
[4] G. Kazantzis, IARC Sci Publ. 71 (1986) 93.
[5] R.W. Seidel, R. Goddard, B. Zibrowius, I.M. Oppel, Polymers 3 (2011) 1458.
[6] E.J. Gao, Z. Wen, M.C. Zhu, Y. Wang, F.C. Liu, L. Wang, M. Su, Y.X. Zhang, T.D. Sun, S.H. Liu, X.N. Gao, Y. Zhang, Coordinazionnaya Himia (Coordination Chemistry) 36 (10) (2010) 755.
[7] W.-Y. Huang, Z.-L. Chen, H.-H. Zou, D.-C. Liu, F.-P. Liang, Polyhedron 50 (1) (2013) 1.
[8] Cambridge Structural Database, version 5.36 (2014), www.ccdc.cam.ac.uk.
[9] K. Kazuhiro, H. Kazutaka, M. Kazuna, M. Osamu, K. Hisatoshi, Synthesis 17 (2006) 2934.
[10] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.29.9. Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark, J.S. Reid. (R. C. Clark, J. S. Reid, Acta Cryst. A 51 (1995) 887).
[11] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[12] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.29.9. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
[13] D.S. Kopchuk, I.S. Kovalev, A.F. Khasanov, G.V. Zyryanov, P.A. Slepukhin, V.L. Rusinov, O.N. Chupakhin, Mendeleev Commun. 23 (3) (2013) 142.
[14] D.S. Kopchuk, G.V. Zyryanov, I.S. Kovalev, A.F. Khasanov, A.S. Medvedevskikh, V.L. Rusinov, O.N. Chupakhin, Chem. Heterocycl. Compd. 49 (3) (2013) 500.
[15] (a) X. Fan, C. Wang, J. Li, G. Zhang, Z. Anorg. Allg. Chem. 641 (6) (2015) 1169;
(b) Y.Q. Sun, J. Hu, H.H. Zhang, Y.P. Chen, J. Solid State Chem. 186 (2012) 189;
(c) F. Jin, H.-Z. Wang, Y. Zhang, Y. Wang, J. Zhang, L. Kong, F.-Y. Hao, J.-X. Yang, J.-Y. Wu, Y.-P. Tian, H.-P. Zhou, Cryst. Eng. Commun. 15 (2013) 3687;
(d) R. Alizadeh, V. Amani, Inorg. Chim. Acta 443 (2016) 151.
[16] R.D. Hancock, Chem. Soc. Rev. 42 (2013) 1500.