ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 2, pp. 92–96. © Pleiades Publishing, Ltd., 2019.
Russian Text © A.F. Khasanov, P.A. Slepukhin, D.S. Kopchuk, A.P. Krinochkin, I.S. Kovalev, G.V. Zyryanov, G.A. Kim, V.L. Rusinov, O.N. Chupakhin, 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 2, pp. 79–83.

Complex of Cadmium(II) Iodide with 3,4-Diphenyl-1-(Pyridin-2-Yl)-6,7-Dihydro-5*H*-Cyclopenta[*c*]pyridine: Synthesis and X-ray Diffraction Study

A. F. Khasanov[a, b], **P. A. Slepukhin**[a, b, *], **D. S. Kopchuk**[a, b], **A. P. Krinochkin**[a, b], **I. S. Kovalev**[b], **G. V. Zyryanov**[a, b], **G. A. Kim**[a], **V. L. Rusinov**[a, b], **and O. N. Chupakhin**[a, b]

[a] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*
[b] *Ural Federal University, Yekaterinburg, Russia*
**e-mail: slepukhin@ios.uran.ru*

Received April 2, 2018; Revised May 18, 2018; Accepted June 15, 2018

Abstract—The structure of the cadmium(II) iodide complex with 3,4-diphenyl-1-(pyridin-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine is studied and determined by X-ray diffraction analysis (CIF file CCDC no. 1833097). The problem about the possibility of coordination of the phenyl substituents of the ligands to the central cadmium atom is examined. The degree of participation of the π system of the phenyl substituent of the ligand in the coordination to the central ion is analyzed using quantum chemical calculations.

Keywords: cadmium(II) iodide, 2,2'-dipyridyl derivatives, complex formation, X-ray diffraction analysis

DOI: 10.1134/S1070328419010032

INTRODUCTION

The chemistry of coordination compounds of cadmium at present attracts special attention because of a high biological toxicity of these compounds and related environmental problems [1–4]. In addition, the coordination polymers with promising applied properties can be built from the cadmium complexes [5]. The cadmium complexes based on the bipyridine derivatives are interesting due to their photophysical characteristics [6, 7].

Nowadays about 150 structures of the cadmium complexes based on the 2,2'-bipyridine type ligands are presented in the Cambridge Structural Database [8]. In most cases, the derivatives of phenanthrolines were used as ligands rather than those of 2,2'-bipyridines (2,2-Bipy). We have previously considered the structures of three cadmium complexes based on (poly)aryl-substituted 2,2-Bipy (according to the X-ray diffraction data) [9]). The Cd–N bond length was shown to depend on the structure of the organic ligand. In terms of this work, we studied the structure of the complex based on 3,4-diphenyl-1-(pyridin-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (L^1) with CdI_2 by X-ray diffraction analysis and compared the examined structure with a series of the earlier described cadmium complexes.

EXPERIMENTAL

This work was carried out using the equipment of the Center for Collective Use “Spectroscopy and Analysis of Organic Compounds.”

^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz) using $SiMe_4$ as an internal standard. Melting points were measured on a Boëtius instrument. Mass spectra (electrospray ionization) were recorded on a MicrOTOF-Q II instrument (Bruker Daltonics) (Bremen, Germany). Elemental analysis was conducted on a PE 2400 II CHN analyzer (Perkin-Elmer). 3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (L^2) was obtained according to an earlier described method [10].

Synthesis of L^1. A mixture of L^2 (345 g, 1.1 mmol) and 1-morpholinocyclopentene (0.89 mL, 5.5 mmol) was stirred at 200°C in an argon atmosphere for 2 h under solvent-free conditions. Then an additional portion of 1-morpholinocyclopentene (0.45 mL, 2.75 mmol) was added, and the mixture was stirred for 1 h under the same conditions. The product was purified by column chromatography using hexane and then ethyl acetate as eluents. The solvent was removed from the product-containing fractions under reduced pressure. The residue was treated with ethanol, and the formed precipitate was filtered off, washed with alcohol, and dried. An analytical sample was obtained by recrystallization from ethanol. The yield was 265 mg (0.76 mmol, 69%), mp = 172–174°C.

^{1}H NMR ($CDCl_3$), δ, ppm: 2.05–2.14 (m, 2H, 6-CH_2), 2.84 (t, 2H, $^3J = 7.6$ Hz, 7-CH_2), 2.53 (t, 2H, $^3J = 7.6$ Hz, 5-CH_2), 7.13–7.22 (m, 5H, Ph), 7.24–7.33 (m, 3H, Ph, H-5 (Py)), 7.38–7.44 (m, 2H, Ph), 7.80–7.86 (ddd, 1H, $^3J = 8.0$, 8.0, and 2.0 Hz, H-4 (Py)), 8.39 (d, 1H, $^3J = 7.8$ Hz, H-3 (Py)), 8.72 (d, 1H, $^3J = 4.8$ Hz, H-6 (Py)). MS m/z (I_{rel}, %): 349.17 $[M + H]^+$ (100), calculated 349.17.

For $C_{25}H_{20}N_2$

Anal. calcd., %	C, 86.17	H, 5.79	N, 8.04
Found, %	C, 86.02	H, 5.88	N, 7.88

Synthesis of (3,4-diphenyl-1-(pyridin-2-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]-pyridine)diiodocadmium(II) (I) · $2CH_3CN$. The crystals of complex **I** suitable for X-ray diffraction analysis were obtained by the slow evaporation of a solution of ligand L^1 (20 mg) and CdI_2 (21 mg, 1 equiv) in acetonitrile (5 mL).

For $C_{29}H_{26}N_4I_2Cd$

Anal. calcd., %	C, 43.72	H, 3.29	N, 7.03
Found, %	C, 43.65	H, 3.36	N, 7.11

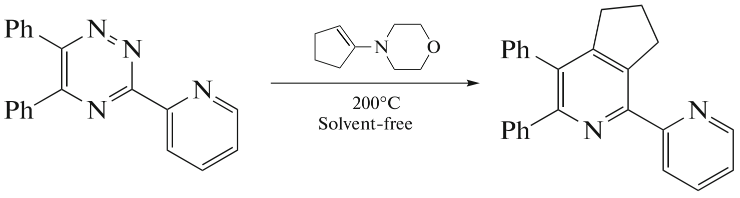
X-ray diffraction analysis of complex **I** was conducted on an Xcalibur 3 automated four-circle diffractometer with a CCD detector using a standard procedure (MoK_α radiation, graphite monochromator, ω scan mode with an increment of 1° at $T = 295(2)$ K). An empirical absorption correction was applied ($\mu(MoK_\alpha) = 2.815$ mm^{-1}). The data were collected and processed using the CrysAlisPro program package [11]. The structure was solved and refined using the OLEX [12] program and the SHELX program package [13]. Non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were placed in the geometrically calculated positions and included into refinement in the isotropic approximation by the riding model with the dependent isotropic thermal parameters. The results of structure refinement and selected crystallographic parameters are the following: monoclinic crystal, $a = 16.7324(9)$, $b = 8.1348(4)$, $c = 23.0488(11)$ Å, $\beta = 107.384(6)°$, $V = 2994.0(3)$ Å^3, space group $P2_1/n$, $FW = 796.74$, $Z = 4$. The number of reflections collected in the range of scattering angles $3.7° < 2\theta < 61.58°$ was 16300, and 8129 of them were independent ($R_{int} = 0.0374$), including 4939 with $I > 2\sigma(I)$. The final parameters for structure refinement are as follows: $R_1 = 0.0994$, $wR_2 = 0.1338$ (all reflections); $R_1 = 0.0492$, $wR_2 = 0.1004$ ($I > 2\sigma(I)$), GOOF on F^2 is 1.018. The peaks of the residual electron density are 0.93/–1.18 e Å^{-3}.

The X-ray diffraction analysis data were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1833097; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Ab initio quantum chemical calculations were performed using the Orca 4.0.1 program in the def2-TZVP basis set. No geometry optimization was carried out, and the three-dimensional model was taken from the X-ray diffraction data.

RESULTS AND DISCUSSION

Ligand L^1 was obtained using the previously described "1,2,4-triazine" methodology [14, 15] by the inverse electron-demand aza-Diels–Alder reaction of 1,2,4-triazine L^2 (diene) [10] and 1-morpholinocyclopentene (dienophile) at 200°C under solvent-free conditions according to the following scheme.



(L^2) (L^1)

The crystals of cadmium complex **I** with ligand L^1 were obtained by crystallization from a saturated solution in acetonitrile using slow evaporation at room temperature. According to the X-ray diffraction data, the mononuclear neutral complex $Cd(L^1)I_2$ (Fig. 1) crystallizes in the centrosymmetric space group as a solvate with two CH_3CN molecules, which do not enter into the nearest coordination sphere of the complexing agent. The coordination polyhedron of the Cd atom is a distorted tetrahedron close to a trigonal pyramid. The cadmium atom deviates from the plane of the atoms I(1)I(2)N(8) by 0.268 Å. The bond lengths are Cd(1)–I(1) 2.7213(6), Cd(1)–I(2) 2.7148(6), Cd(1)–N(8) 2.305(4), and Cd(1)–N(1) 2.300(5) Å, they do not demonstrate significant deviations from the standard values, and the lengths of two Cd–N bonds are the same within the experimental inaccuracy. Ligand L^1 is a typical chelating agent of the α,α-

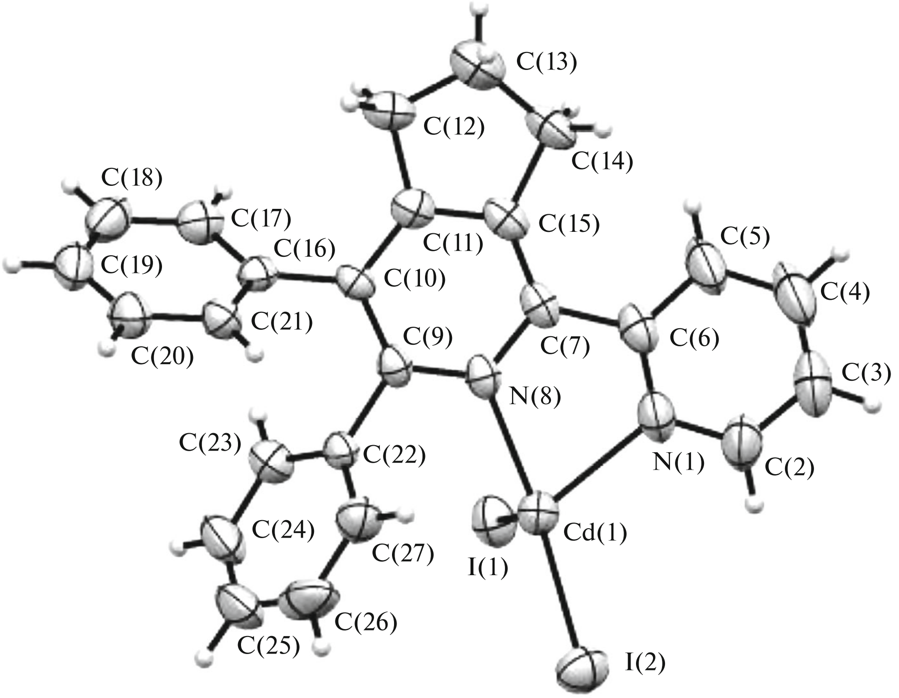


Fig. 1. Structure of complex **I** (according to the X-ray diffraction data) in thermal ellipsoids of 50% probability.

dipyridyl type, and the chelate bond angle N(1)Cd(1)N(8) is 70.89(16)°. The cadmium atom shifts from the plane of the atoms N(1)C(6)C(7)N(8) by 0.441 Å. The C(6)–C(7) bond length in the metallochelate cycle (1.507 Å) indicates an insignificant conjugation effect of the π systems of the pyridyl rings.

Both phenyl substituents in a molecule of compound **I** are unfolded by 60° to the plane of the pyridine cycle. The distance for the atoms of the phenyl substituents C(16)···C(22) is 2.95 Å, which allows one to speak about the partial overlapping of the π systems of the latter. Taking into account the shortened intermolecular contact between the phenyl substituents of the adjacent molecules C(25)···C(25) ($-x$, $2 - y$, $1 - z$) equal to 3.354 Å, one can assume the π-stacking interaction in the ensembles of four phenyl rings of the molecular crystal packing.

It is most likely that the deviation from the tetrahedral configuration of cadmium cannot be explained only by the steric influence of the bulky substituents, especially with allowance for the fact that the van der Waals radii of the iodine atoms and carbon atoms of the phenyl rings in the molecule are not overlapped. No tetracoordination was observed earlier for the CdI_2 complexes with the ligands of the α,α-dipyridyl type (the coordination number of cadmium was 4) [8], and the structural diversity was restricted by penta- and hexacoordinated complexes. The interatomic distance C(27)···Cd(1) (3.188 Å) between the central ion and phenyl substituent assumes a considerable overlapping of the aromatic π system with the electronic shell of cadmium and the formation of a bond according to the "sandwich" structure type. In this case, the central Cd^{2+} ion gains fairly usual distorted trigonal bipyramidal configuration, which explains the observed arrangement of the substituents of the nearest coordination sphere. A similar type of interaction has previously been observed for the cadmium complexes with the porphyrinoid ligands [16].

In fact, the calculation using the quantum mechanical method showed the overlapping of the electron density of the 121st molecular orbital with an energy of –7.23 eV between the Cd atom and phenyl ring for the value of the isodensity surface <0.028 (Fig. 2). No similar overlapping was revealed for other molecular orbitals.

Thus, the interaction of the central atom with the π system of the phenyl substituent is intermediate between a simple van der Waals contact and the formation of the full-value π complex according to the metallocene type.

The molecular packing in the crystal is ladder-parquet. There are significant pores oriented along the 0*b* axis and filled by the solvent (CH_3CN) molecules (Fig. 3). No substantially shortened intermolecular contacts are observed in the crystal.

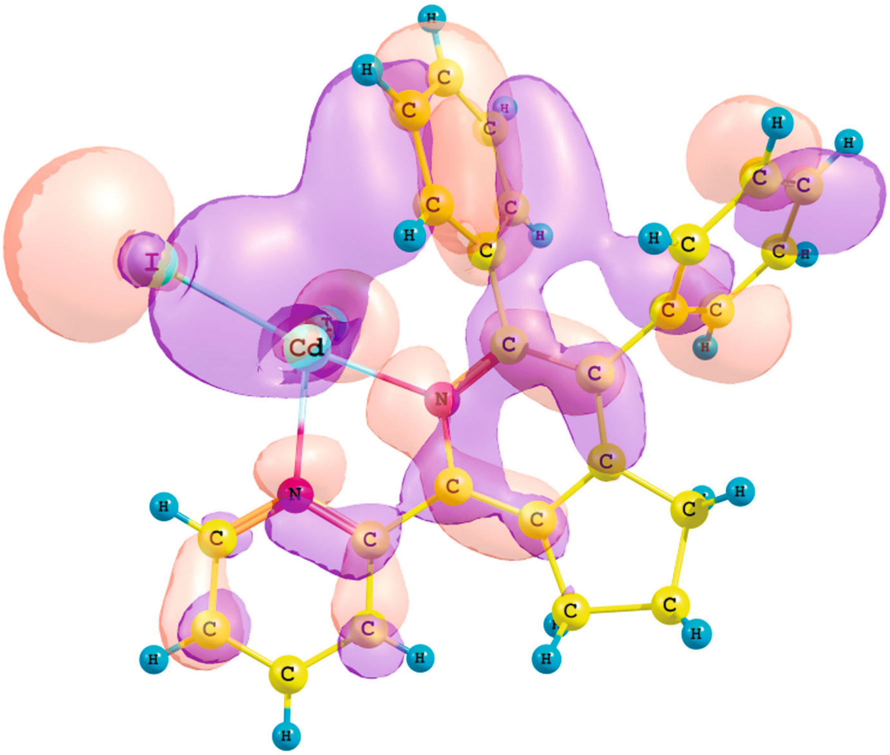


Fig. 2. The 121st molecular orbital of compound **I** (the value for the isodensity surface is 0.02).

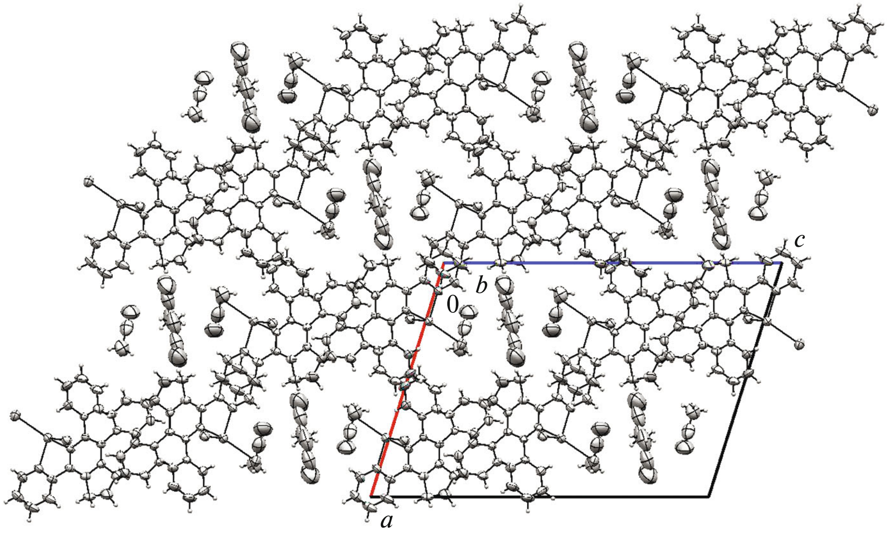


Fig. 3. Fragment of the crystal packing of complex **I** according to the X-ray diffraction data.

ACKNOWLEDGMENTS

This work was carried out in the framework of the program of scientific studies of the Postovskii Institute of Organic Synthesis (Ural Branch, Russian Academy of Sciences) (project no. 115030310087 0398-2014-0030) and supported by the Russian Science Foundation (project no. 18-73-10119).

REFERENCES

1. Duruibe, J.O., Ogwuegbu, M.O.C., and Egwurugwu, J.N., *Intern. J. Phys. Sci.*, 2007, vol. 2, no. 5, p. 112.
2. Verma, R. and Dwivedi, P., *Recent Res. Sci. Technol.*, 2013, vol. 5, no. 5, p. 98.
3. Pinot, F.I., Kreps, S.E., Bachelet, M., et al., *Rev. Environ. Health*, 2000, vol. 15, no. 3, p. 299.

4. Kazantzis, G., *IARC Sci. Publ.*, 1986, vol. 71, p. 93.
5. Seidel, R.W., Goddard, R., Zibrowius, B., and Oppel, I.M., *Polymers*, 2011, vol. 3, p. 1458.
6. Kumara, R., Bhargava, P., and Dvivedi, A., *Proc. Mater. Sci.*, 2015, vol. 10, p. 37.
7. Suna, X.-Z., Huangc, Z.-L., Wangc, H.-Z., et al., *Z. Anorg. Allg. Chem.*, 2005, vol. 631, p. 919.
8. Cambridge Structural Database. Version 5.39, 2017.
9. Kopchuk, D.S., Slepukhin, P.A., Kovalev, I.S., et al., *Polyhedron*, 2016, vol. 110, p. 235.
10. Case, F.H., *Org. Chem.*, 1965, vol. 30, p. 931.
11. CrysAlisPro. Version 1.171.36.28, Agilent Technologies.
12. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallorg.*, 2008, vol. 64, p. 112.
14. Pabst, G.R. and Sauer, J., *Tetrahedron Lett.*, 1998, vol. 39, p. 6687.
15. Rykowski, A., Branowska, D., and Kielak, J., *Tetrahedron Lett.*, 2000, vol. 41, p. 3657.
16. Stepién, M. and Latos-Grazyñski, L., *J. Am. Chem. Soc.*, 2002, vol. 124, no. 15, p. 3838.

Translated by E. Yablonskaya