ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2349–2351. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © L.A. Antina, N.A. Dudina, G.B. Guseva, M.B. Berezin, A.I. V'yugin, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 11, pp. 1898–1900.

Synthesis and Photophysical Properties of Cd(II) and Cu(II) Complexes with Decamethylated Bis(dipyrrolylmethene)

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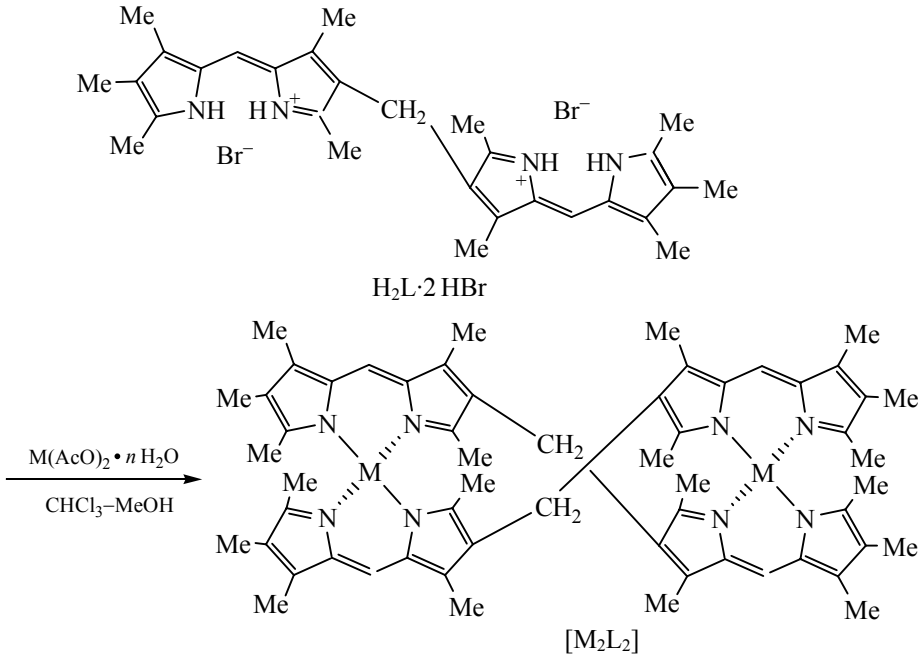
Received October 14, 2010

Abstract—Copper(II) and cadmium(II) complexes with bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)-methane were synthesized. Influence of the complex-forming ion nature on the optical properties of $[Cd_2L_2]$ and $[Cu_2L_2]$ helicates was studied.

DOI: 10.1134/S1070363211110211

Earlier [1, 2] zinc(II) complexes with a series an bis-(dipyrrolylmethenes), $[Zn_2L_2]$, which possess intensive fluorescence in non-polar solvents, have been synthesized and studied by spectral methods. To study the influence of the nature of a complex-forming metal on the optical properties of coordination compounds of bis(dipyrrolylmethenes), we have synthesized cadmium(II) and copper(II) complexes with bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane, (H_2L)–$[M_2L_2]$.

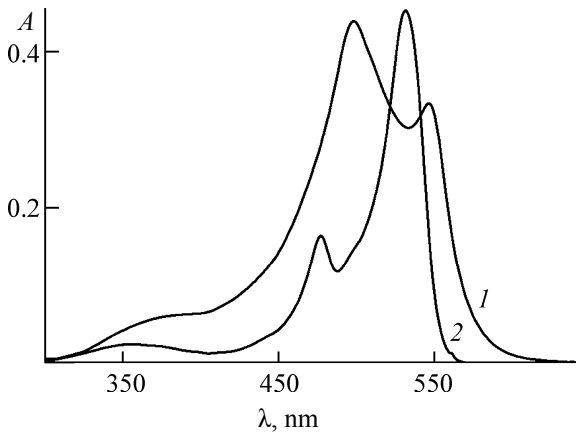
Helicates of $[Cd_2L_2]$ and $[Cu_2L_2]$ were prepared by the exchange reaction of Cd(II) and Cu(II) acetates with the dihydrobromide ($H_2L \cdot 2HBr$) of a corresponding ligand in a chloroform–methanol mixture in the presence of triethylamine.



$H_2L \cdot 2\,HBr$

$[M_2L_2]$

M = Cd(II), Cu(II).



Electron absorption spectra of (*1*) $[Cu_2L_2]$ and (*2*) $[Cd_2L_2]$ complexes in benzene.

The nature of a complex-forming ion noticeably affects spectral characteristics of electronic absorption spectra (EAS) and emission spectra of the synthesized complexes. The electron absorption spectra of solutions of Cd_2L_2 complexes are similar to the spectra of Zn(II) and Hg(II) helicates with analogous composition and structure [3, 4, 5]. One intensive band with λ_{max} 526 nm, a much less intensive band at 477 nm, and a weak widened charge-transfer band (CTB) at 367 nm (see the figure) are present in EAS of the complex $[Cd_2L_2]$ in benzene. The complex $[Cd_2L_2]$ shows intensive fluorescence in non-polar and low-polar organic solvents, but its quantum yield is several times lower than for the zinc(II) complex with similar composition, which was studied before [3, 4]. The highest fluorescence quantum yield (φ 0.27) was obtained in cyclohexane, whereas in other non-polar solvents (benzene, hexane, and heptane) the value of φ is in the limits of 0.12–0.16. Stokes shift reaches 12–14 nm. In polar solvents (chloroform and alcohols) a sharp decrease in the fluorescence quantum yield is observed (up to zero). The helicate $[Cd_2L_2]$ is stable in non-polar and low-polar solvents, but decomposes in polar electron-donor solvents (dimethyl formamide and pyridine): within several days the characteristic bands of the complex decrease and disappear from the spectrum of the solution, and absorption in the near-ultraviolet region of the spectrum increases, apparently owing to the formation of monopyrrole derivatives.

The feature of electron spectra of the complex $[Cu_2L_2]$ in the studied organic solvents (see the figure), in contrast to zinc(II), cadmium(II), mercury(II), and cobalt(II) helicates with similar structures [3, 4, 5], consists in the fact that there are two intensive bands in its spectra. In EAS of a solution of the complex in benzene the ratio of ε values for the bands at λ_{max}^{495} and λ_{max}^{539} nm is ~1.3. The replacement of the polar electron-donor solvent DMF by non-polar benzene causes a small (~4 nm) bathochromic shift of the maximum of the first absorption band. Unlike the cadmium(II) helicate, the fluorescence of the complex $[Cu_2L_2]$ is completely quenched in organic solvents. The complex $[Cu_2L_2]$ is stable both in non-polar and in polar electron-donor solvents.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Bruker 500 NMR spectrometer. The electron absorption and fluorescence spectra of samples in organic solvents were taken on an SF-103 spectrophotometer (Akvilon, Russia) and an SM 2203 (SOLAR) spectrophotometer. Organic solvents (chemically-pure grade) were additionally purified according to the known procedures [6]. According to the results of titration by Fisher's method, water contents in solvents did not exceed 0.02%.

High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument by the electrospray ionization method (ESI) [7]. High-resolution mass spectra were measured in the Department of structural researches of Institute of Organic Chemistry of Russian Academies of Sciences (Moscow).

Cu(II) complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane, $[Cu_2L_2]$. Dihydrobromide of the ligand (0.200 g, 0.332 mmol) was dissolved in 15 ml of methanol with heating and stirring, then 0.034 g (0.332 mmol) of triethylamine and 0.331 g of a solution of $Cu(AcO)_2 \cdot H_2O$ (1.66 mmol) in 30 ml of methanol was added. The mixture was boiled within 1 h and then cooled. The dropped precipitate was filtered off, washed on a filter by a great amount of water, methanol, and ether, and dried up in air at room temperature. The residuum was dissolved in methylene chloride and chromatographed on silicagel (100/250), the eluent was distilled off, and the complex was isolated and additionally dried up under low pressure. Yield 76.2%. Electron absorption spectra, λ_{max}, nm (log ε): (C_6H_6), 539 (4.91), 495 (5.04), 388–397 (4.28); ($CHCl_3$), 536 (4.90), 497 (5.03), 386–398 (4.24). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.01 s (12H, CH_3), 2.15 s (12H, CH_3), 2.27 s

(12H, CH_3), 2.56 s (12H, CH_3), 2.64 s (12H, CH_3), 3.58 s (4H, CH_2), 7.03 s (4H, CH_{meso}). Mass spectrum, *m/z*: 1003.40 $[M + H]^+$, calculated 1003.42 $[M + H]^+$. $C_{58}H_{68}Cu_2N_8$.

Cu(II) complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane, $[Cd_2L_2]$. Dihydrobromide of the ligand (0.10 g, 0.165 mmol) was dissolved in 10 ml of chloroform, 0.017 g (0.165 mmol) of triethylamine was added with stirring, and, 3 min later, a solution of 0.283 g (1.06 mmol) of $Cd(AcO)_2 \cdot 2H_2O$ in 20 ml of methanol (color of the solution changes from yellow to red-green). The solution was stirred for 1 h, and then washed out 3 times with water in a separatory funnel. A chloroform layer was separated, dried by Na_2SO_4, evaporated, and the complex was precipitated by hexane. Yield 81%. Electron absorption spectra, λ_{max}, nm: (C_6H_6), 526, 477, 367 (CTB); (C_7H_{16}), 521, 475, 356 (CTB). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (12H, CH_3), 2.15 s (12H, CH_3), 2.18 s (12H, CH_3), 2.30 s (12H, CH_3), 2.35 s (12H, CH_3), 3.58 s (4H, CH_2), 7.03 s (4H, CH_{meso}). Mass spectrum, *m/z*: found 1005.36 $[M + H]^+$, calculated 1005.37 $[M + H]^+$. $C_{58}H_{68}Cd_2N_8$.

ACKNOWLEDGMENTS

This work was supported by the analytical departmental target program "Development of the scientific potential of the higher school" (2009–2010, project no. 2.1.1/827) and by the federal target program "Scientific and educational-scientific personnel of innovation Russia" for 2009–2013 (state contract no. 02.740.11.0253).

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