ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 3, pp. 591–593. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © L.A. Antina, N.A. Dudin, M.B. Berezin, G.B. Guseva, E.V. Antina, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 3, pp. 496–498.

# Synthesis and Spectral Properties of the Nickel(II) and Mercury(II) Helicates with 3,3'-Bis(dipyrrolylmethenes)

**L. A. Antina, N. A. Dudin, M. B. Berezin, G. B. Guseva, and E. V. Antina**

*Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
*e-mail: eva@iss-ras.ru*

Received July 8, 2010

**Abstract**—The influence of the nature of the complexing metal on the optical properties of coordination compounds of bis(dipyrrolilmethenes) was studied.

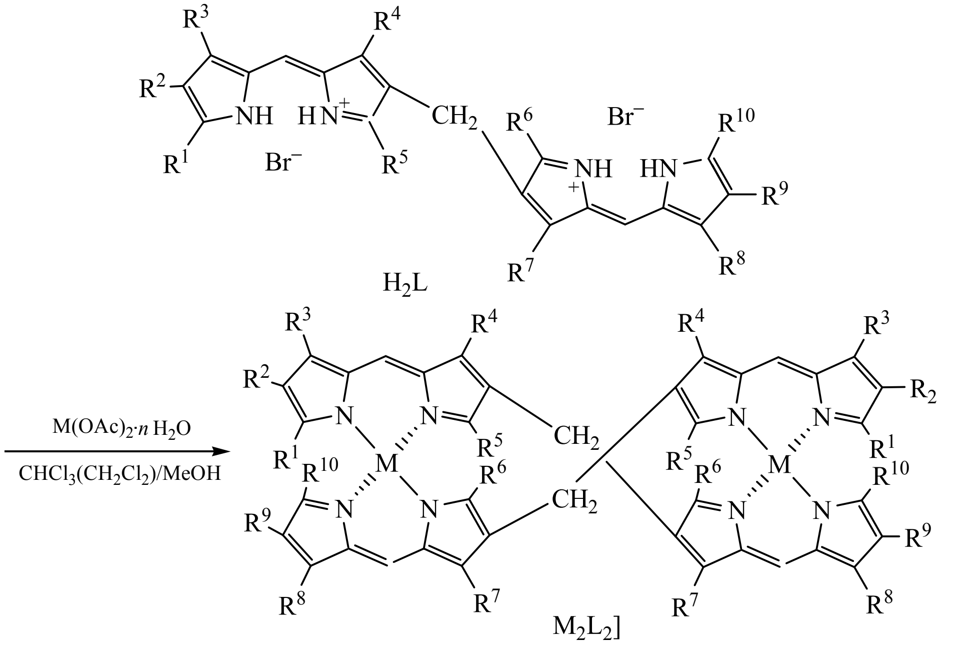
**DOI:** 10.1134/S1070363211030261

Among the unique set of practically important properties of the of 3,3'-bis(dipyrrolylmethene) ligands the most important one is their structural preorganization favorable for the formation of stable neutral helicates, which are of a considerable interest for supramolecular coordination chemistry and, in addition, possess a set of practically important spectral properties [1, 2] providing a broad prospects for their use as a chromophore/fluorescent sensors and tags [3, 4].

Previously, we synthesized and studied by spectral methods the zinc(II) complexes with a number of bis(dipyrrolylmethenes), [$Zn_2L_2$] [4, 5] showing an intense fluorescence in nonpolar solvents. In order to study the influence of the nature of the complex-forming metal on the optical properties of coordination compounds of bis(dipyrrolylmethenes) we have synthesized the nickel(II) complexes with bis(1,3,7,9-tetramethyl-2-ethyldipyrrolylmethen-8-yl)methane, and mercury(II) complexes with bis(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)methane ($H_2L$) of the [$M_2L_2$] composition.

The complexes [$Ni_2L_2$] and [$Hg_2L_2$] were prepared by the reaction of the respective metal acetates with alkyl-substituted 3,3'-bis(dipyrrolylmethene) hydrobro-

---



[$Ni_2L_2$]: L = $R^1$, $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^{10}$ = $CH_3$; $R^2$, $R^9$ = $C_2H_5$; [$Hg_2L_2$]: L = $R^1$, $R^2$, $R^3$, $R^4$, $R^5$, $R^6$, $R^7$, $R^8$, $R^9$, $R^{10}$ = $CH_3$.

mides ($H_2L·2HBr$) in a mixture of chloroform (or dichloromethane)–methanol in the presence of triethylamine according to the scheme above.

The methods of synthesis and spectral properties of the helicand hydrobromides ($H_2L·2HBr$) used in the syntheses have been published earlier [6, 7].

The electron absorption spectra (EAS) of each complex [$Ni_2L_2$] and [$Hg_2L_2$] in cyclohexane contain one strong band at $\lambda_{max}$ (log ε), respectively, 550 (4.94) and 524 (–) nm, a less intense band at 462 and 476 nm, and a low intensity broad charge transfer band in the region of 365–400 nm (see the figure), which correspond to the three electronic transitions ($S_0$–$S_1$, $S_0$–$S_2$, and $S_0$–$S_3$), as shown in [8]. The EAS appearance of the helicates [$Ni_2L_2$] and [$Hg_2L_2$] solutions is consistent with the published data on the EAS of the *d*-metal complexes with structurally related bis(dipyrrolylmethenes) of similar composition [9, 10].

In the EAS in DMF and chloroform occurs a slight blue shift (1–7 nm) of the first strong absorption maximum in comparison with the spectrum in cyclohexane.

The emission spectra of the complex [$Hg_2L_2$] in cyclohexane, hexane, heptane, benzene, and chloroform are practically mirror reflections of the absorption spectra (see the Fig. 1a). In nonpolar solvents, the fluorescence quantum yield ($\Phi_{fl}$) is significantly higher than in the polar ones (in cyclohexane $\Phi_{fl}$ reaches ~ 0.03, in DMF is close to zero), which allows us to consider the complex as a fluorescent sensor of the medium polarity. The same pattern of the environment polarity effect on the $\Phi_{fl}$ value was observed earlier for the [$Zn_2L_2$] complexes. However, [$Hg_2L_2$] shows a much smaller quantum yield in these solvents in comparison with the [$Zn_2L_2$] complexes showing $\Phi_{fl}$ that reaches ~1.0 in cyclohexane, 0.6 in benzene, 0.08 in chloroform, 0.02 in PrOH, and ~0.004 in DMF [4]. Furthermore, in contrast to [$Zn_2L_2$], in the case of [$Hg_2L_2$] fluorescence quenching is observed in benzene: the value of $\Phi_{fl}$ is reduced to ~0.003. The analysis of the EAS of [$Hg_2L_2$] solution in $C_6H_6$ showed that the complex decomposed in time to a colored intermediate with a subsequent decoloration of the solution, which may be due to the specific interactions Hg(II)–$C_6H_6$ and the mercuration processes [11, 12].

The complex [$Ni_2L_2$] is stable in solution under light. But, unlike the zinc(II) and mercury(II) helicates of the same composition, we observed complete quenching of the [$Ni_2L_2$] complex fluorescence in organic solvents.

## EXPERIMENTAL

**Ni(II) complex with bis(1,3,7,9-tetramethyl-2-ethyldipyrrolylmethene-8-yl)methane, [$Ni_2L_2$].** 0.093 g (0.147 mmol) of the ligand was dissolved in 10 ml of chloroform, and at stirring 0.12 g (1.16 mmol) of triethylamine was added, then a solution of 0.192 g (0.77 mmol) of $Ni(AcO)_2·4H_2O$ in 10 ml of methanol (solution color changed from yellow to purple-red). The solution was stirred for 24 h, then washed 3 times with water in a separatory funnel to remove the water-soluble impurities. The chloroform layer was separated, dried over sodium sulfate, and evaporated. The complex was dissolved in benzene and subjected to

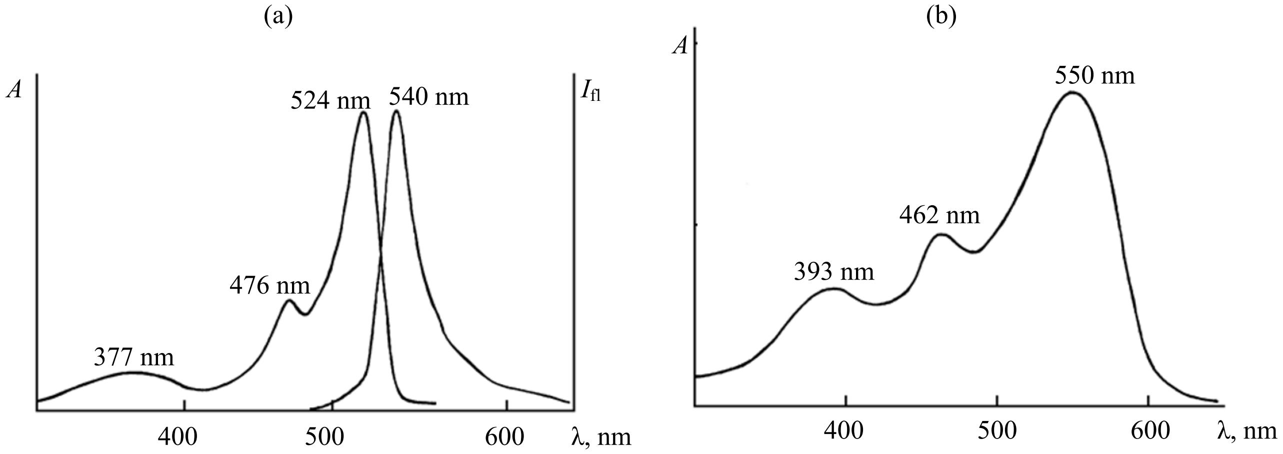


**Fig. 1.** (a) Electron absorption and emission spectra of the complex of mercury(II) with bis(1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl)-methane [$Hg_2L_2$] and (b) electron absorption spectrum of the complex of nickel(II) with bis(1,3,7,9-tetramethyl-2-ethyldipyrrolylmethene-8-yl)methane [$Ni_2L_2$] in $C_6H_{12}$.

chromatography on silica gel (40/100), eluent benzene. Yield 71%. $\lambda_{max}$, nm: 547, 462, 396 (charge transfer peak) (DMF) and 549, 466 (shoulder), 394 (charge transfer peak) ($CHCl_3$). The $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.10 m (12H, $CH_2CH_3$), 2.14 s (12H, $CH_3$), 2.29 s (12H, $CH_3$), 2.45 q ( 8H, $CH_2CH_3$), 2.56 s (12H, $CH_3$), 2.67 s (12H, $CH_3$), 3.58 s (4H, $CH_2$ spacer), 7.04 s (2H, CH-*meso*), 7.07 s (2H, CH-*meso*). Mass spectrum, *m/z*: 1049.50 $[M + H]^+$, 1068.48 $[M + NH_4]^+$. Found, %: P 70.44, H 7.23, N 10.50. $C_{62}H_{76}N_8Ni_2$. Calculated, %: C 70.87, H 7.29; N 10.66.

**The Hg(II) complex with bis(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)methane, $[Hg_2L_2]$**. 0.130 g (0.216 mmol) of the ligand was dissolved in 20 ml of methylene chloride and 0.11 g (1.06 mmol) of triethylamine, and then a solution of 1.037 g (2.923 mmol) of $Hg(AcO)_2$ in 20 ml of methanol was added to the mixture at stirring (the solution color changed from brown to red). The mixture was stirred for 1 h, the formed solution of the complex in methylene chloride was cooled, filtered, then washed several times with water to remove methanol and salts. Organic layer was separated, dried over sodium sulfate, and then the solvent was evaporated under a reduced pressure, and the residue was dried in air. Yield 89%. $\lambda_{max}$, nm: 519, 476 (shoulder), 365 (charge transfer peak) (DMF), and 520, 480 (shoulder), 370 (charge transfer peak) ($CHCl_3$). The $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 1.99 s (12H, $CH_3$), 2.12 s (12H, $CH_3$), 2.13 s (12H, $CH_3$), 2.25 s (12H, $CH_3$), 2.58 s (12H, $CH_3$), 3.42 s (4H, $CH_2$ spacer), 6.99 s (4H, CH-*meso*). Mass spectrum, *m/z*: 1279.49 $[M + H]^+$, 1296.49 $[M + NH_4]^+$. Found, %: C 54.19, H 5.27; N 8.47. $C_{58}H_{68}N_8Hg_2$. Calculated, %: C 54.49, H 5.36; N 8.77.

The $^1H$ NMR spectra were taken from the solutions in deuterated chloroform ($CDCl_3$) on a Bruker 500 NMR spectrometer. Electron absorption and fluorescence spectra of samples dissolved in organic solvents were obtained on a SF-103 (Aquilon, Russia) and a CM 2203 (SOLAR) spectrometers. Organic solvents and reagent were additionally purified according to known methods [13]. The water content in the solvents did not exceed 0.02% according to the results of titration by the Fisher method.

The high resolution mass spectra were recorded on a Bruker micrOTOF II instrument at electrospray ionization (ESI) [14]. Measurements of the high resolution mass spectra were performed in the Department of Structural Research of the Institute of Organic Chemistry, Russian Academy of Sciences, Moscow.

## ACKNOWLEDGMENTS

This work was supported by the Basic Research Program of the Presidium of Russian Academy of Sciences 18-P-2 Project (2010), program “Development of Scientific Potential of Higher School (2009–2010)” (project no. 2.1.1/827), Federal Program “Scientific and scientific-pedagogical personnel of innovative Russia” for 2009–2013 (State contract no. 02.740.11.0253).

## REFERENCES

1. Wood, E. and Thompson, A., *Chem. Rev.*, 2007, vol. 107, p. 1831.
2. Cato, A., *New Developments in Organometallic Chemistry Research*, Nova Science Publishers, 2006, p. 63.
3. Lakovich, J., *Osnovy fluorestsentnoi spektroskopii* (Fundamentals of Fluorestsent Spectroscoly), Moscow: Mir, 1986.
4. Dudina, N.A., Antina, L.A., Guseva, G.B., Berezin, M.B., and V’yugin, A.I., Abstract of Papers, *12th Conf. of Yang Scientists on Organic Chemistry*, Suzdal’, December 7–11, 2009, p. 248.
5. Antina, E.V., Berezin, M.B., Dudina, N.A., Guseva, G.B., Antina, L.A., and V’yugin, A.I., *Zh. Obshch. Khim.*, 2010, vol. 80, no. 6, p. 1048.
6. Guseva, G.B., Dudina, N.A., Antina, E.V., V’yugin, A.I., and Semeikin, A.S., *Zh. Obshch. Khim.*, 2008, vol. 78, no. 6, p. 987.
7. Antina, E.V., Guseva, G.B., Dudina, N.A., V’yugin, A.I., and Semeikin, A.S., *Zh. Obshch. Khim.*, 2009, vol. 79, no. 11, p. 1903.
8. Li, W., Wang, Y.-B., Yang, L.-Y., Shan, X.-F., Cai, X., Szeghalm, A., Ye Y., Ma, J.- S., Luo, M.-D., Hu, J., and Kiefer, W., *J. Phys. Chem.*, 2006, vol. 110, p. 21958.
9. Yang L., Zhang Y., Yang G., Chen Q., and Ma, J.S., *Dyes and Pigments*, 2004, vol. 62, p. 27.
10. Thompson, A. and Dolphin, D., *J. Org. Chem.*, 2000, vol. 65, p. 7870.
11. *Obshchaya organicheskaya khimiya* (Comprehensive Organic Chemistry), Barton, D. and Ollis, W.D., Eds, Moscow: Khimiya, 1984, vol. 7, pp. 73–95.
12. Poson, P., *Khimiya metalloorganicheskikh soedinenii* (Chemistry of Organometallic Compounds), Beletskaya, I.P., Ed., Moscow: Mir. 1970.
13. Gordon, A.J. and Ford, R.A., *The Chemist’s Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
14. Belyakov, P.A., Kadentsev, V.I., Chizhov, A.O., Kolotyrkina, N.G., Shashkov, A.S., and Ananikov, V.P., *Mendeleev Commun.*, 2010, vol. 20, p. 125.