ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 6, pp. 1216–1218. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.V. Antina, M.B. Berezin, N.A. Dudina, G.B. Guseva, L.A. Antina, A.I. V'yugin, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 6, pp. 1048–1050.

LETTERS TO THE EDITOR

Synthesis and Spectral Properties of Zinc(II) Helicates with 3,3'-Bis(dipyrrolylmethenes) Series

E. V. Antina, M. B. Berezin, N. A. Dudina, G. B. Guseva, L. A. Antina, and A. I. V'yugin

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

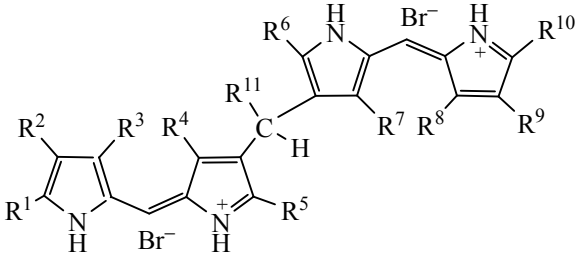
Received December 24, 2009

DOI: 10.1134/S1070363210060332

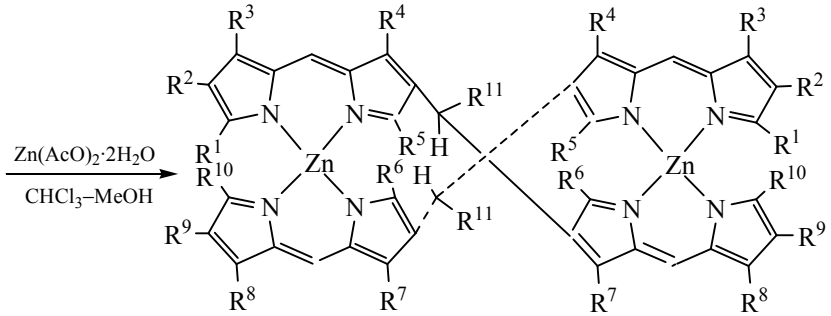
The creation of the fundamentally new, electrically neutral complexes of 3,3'-bis(dipyrrolylmethenes) of spiral-shaped structure [1] is among the promising contemporary trends in the coordination chemistry of linear oligopyrrols. 3,3'-Bis(dipyrrolylmethene) helicates are formed due to covalent and donor–acceptor bonding, contain no counterions that results in their high stability and facilitates their synthesis and chromatographic purification.

We synthesized binuclear homoleptic zinc(II) complexes of composition 2:2 by reaction of zinc acetate dihydrate with seven 3,3'-bis(dipyrrolylmethenes) **I–VII** dihydrobromides in chloroform–methanol medium by the modernized procedure [2].

Electronic absorption (EA) spectra of complexes in organic solvents contain a strong band with a maximum in the range of 498–531 nm, less intensive



I·2HBr–**VII**·2HBr



I, $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = R_9 = R_{10}$= Me, R_{11} = H; **II**, $R_1 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = R_{10}$ = Me, $R_2 = R_9$ = Et, R_{11} = H; **III**, $R_1 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = R_{10}$ = Me, $R_2 = R_9$ = Et, R_{11} = Ph; **IV**, $R_1 = R_2 = R_3 = R_5 = R_6 = R_8 = R_9 = R_{10}$ = Me, $R_4 = R_7$ = Et, R_{11} = H; **V**, $R_1 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = R_{10}$ = Me, $R_2 = R_9 = R_{11}$ = H; **VI**, $R_2 = R_3 = R_4 = = R_5 = R_6 = R_7 = R_8 = R_9$ = Me, $R_1 = R_{10} = R_{11}$ = H; **VII,** $R_4 = R_5 = R_6 = R_7$ = Me, $R_1 = R_2 = R_3 = R_8 = R_9 = R_{10} = R_{11}$ = H.

band at 457–480 nm and a weak broadened band of charge transfer (CTB) in the range of 360–375 nm. Complexes give intensive fluorescence both in the solid phase and in the nonpolar solvents. Fluorescence quantum yield in benzene is 0.56–0.68, in cyclohexane 0.9. Successful combination of practically useful optical (chromophore and fluorescence) properties provides evident possibilities of the use of the obtained zinc(II) helicates as fluorescence markers and medium polarity sensors [3].

Complex of Zn(II) with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane [Zn_2(I)$_2$]. To a solution of 0.18 g (0.298 mmol) of **I**·2HBr in 30 ml of chloroform was added 0.12 g (1.16 mmol) of triethylamine under stirring, and over 3 min a solution of 0.32 g (1.46 mmol) of $Zn(AcO)_2 \cdot 2H_2O$ in 20 ml of methanol was added. The reaction mixture was stirred at room temperature for 1 h. Then it was washed with water 3 times. Chloroform layer was separated, concentrated. The precipitate was filtered off, washed with methanol, dried, dissolved in 5 ml of benzene, and subjected to chromatography on silica gel (40/100), eluent benzene (the first fraction was a bright-crimson fluorescing zone); then with benzene:methanol mixture 10:1 (the second fraction). Yield (the first zone) 0.225 g (74.9%). EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (525; 5.34); 476; 367 (CTB); C_6H_6: (530; 5.48); 478; 369 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 545. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 s (12H, CH_3), 1.92 s (12H, CH_3), 2.00 s (12H, CH_3), 2.19 s (12H, CH_3), 2.22 s (12H, CH_3), 3.41 s (4H, –CH_2–, spacer), 6.89 s (4H, –CH_{meso}–). Found, %: C 69.01; H 6.75; N 11.07. $C_{58}H_{68}N_8Zn_2$. Calculated, %: C 69.11; H 6.80; N 11.12.

Compounds [Zn_2(**II**)$_2$]–[Zn_2(**VII**)$_2$] were obtained similarly.

Complex of Zn(II) with bis(2,4,7,9-tetramethyl-8-ethyldipyrrolylmethen-3-yl)methane [Zn_2(II)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (525; 5.42); 476; 375 (CTB); C_6H_6: (530; 5.46); 478; 370 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 545. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (12H, –CH_2–CH_3), 1.39 s (12H, CH_3), 2.01 s (12H, CH_3), 2.19 s (12H, CH_3), 2.20 s (12H, CH_3), 2.36 q (8H, –CH_2–CH_3), 3.43 s (4H, –CH_2–, spacer), 6.90 s (4H, –CH_{meso}–). Found, %: C 69.87; H 7.17; N 10.48. $C_{62}H_{76}N_8Zn_2$. Calculated, %: C 69.98; H 7.20; N 10.53.

Complex of Zn(II) with bis(3,3',5,5'-tetramethyl-4'-ethyldipyrrolylmethen-4-yl)phenylmethane [Zn_2(III)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (526; 5.45); 477; 374 (CTB); C_6H_6: (531; 5.48); 480; 376 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 548. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (12H, –CH_2–CH_3), 1.50–1.51 d (12H, CH_3), 2.00–2.02 d (12H, CH_3), 2.16–2.17 d (12H, CH_3), 2.21–2.22 d (12H, CH_3), 2.39 q (8H, –CH_2–CH_3), 5.28 s (2H, –CH_2–, spacer), 6.80 s (4H, –CH_{meso}–), 6.94–6.96 d (4H, *m*-CH-Ph), 7.20–7.21 d (4H, *o*-CH-Ph), 7.39 s (2H, *p*-CH-Ph). Found, %: C 73.01; H 6.80; N 9.14. $C_{74}H_{84}N_8Zn_2$. Calculated, %: C 73.08; H 6.96; N 9.21.

Complex of Zn(II) with bis(2,7,8,9-tetramethyl-4-ethyldipyrrolylmethen-3-yl)methane [Zn_2(IV)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (524; 5.33); 477; 368 (CTB); C_6H_6: (529; 5.39); 479; 369 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 545. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (12H, –CH_2–CH_3), 1.43 s (12H, CH_3), 1.91 s (12H, CH_3), 1.97 s (12H, CH_3), 2.20 s (12H, CH_3), 2.65 q (8H, –CH_2–CH_3), 3.49 s (4H, –CH_2–, spacer), 6.89 s (4H, –CH_{meso}–). Found, %: C 69.90; H 7.12; N 10.45. $C_{62}H_{76}N_8Zn_2$. Calculated, %: C 69.98; H 7.20; N 10.53.

Complex of Zn(II) with bis(1,3,7,9-tetramethyldipyrrolylmethen-8-yl)methane [Zn_2(V)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (517; 5.47); 467; 364 (CTB); C_6H_6: (522; 5.52); 470; 365 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 535. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 s (12H, CH_3), 2.05 s (12H, CH_3), 2.23 s (12H, CH_3), 2.31 s (12H, CH_3), 3.43 s (4H, –CH_2–, spacer), 5.98 s (4H, H_β), 6.93 s (4H, –CH_{meso}–). Found, %: C 68.04; H 6.27; N 11.72. $C_{54}H_{60}N_8Zn_2$. Calculated, %: C 68.14; H 6.35; N 11.77.

Complex of Zn(II) with bis(2,3,7,9-tetramethyldipyrrolylmethen-8-yl)methane [Zn_2(VI)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (519; 5.32); 470; 375 (CTB); C_6H_6: (524; 5.37); 474; 371 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 537. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 s (12H, CH_3), 1.99 s (12H, CH_3), 2.22 s (24H, CH_3), 3.40 s (4H, –CH_2–, spacer), 6.98 s (4H, –CH_{meso}–), 7.11 s (4H, H_α). Found, %: C 68.11; H 6.22; N 11.70. $C_{54}H_{60}N_8Zn_2$. Calculated, %: C 68.14; H 6.35; N 11.77.

Complex of Zn(II) with bis(7,9-dimethyldipyrrolylmethen-8-yl)methane [Zn_2(VII)$_2$]. EA spectrum, λ_{max}^{abs} (log ε), nm, DMF: (498; 5.30); 457; 360 (CTB); C_6H_6: (507; 5.31); 457; 361 (CTB). Emission spectrum (C_6H_6), λ_{max}^{fl}, nm: 521. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 s (12H, CH_3), 2.22 s

(12H, CH_3), 3.41 s (4H, $–CH_2–$, spacer), 6.41 s (4H, H), 6.99 s (4H, $–CH_{meso}–$), 7.06 s (4H, H), 7.33 s (4H, H). Found, %: C 65.69; H 5.22; N 13.29. $C_{46}H_{44}N_8Zn_2$. Calculated, %: C 65.80; H 5.28; N 13.35.

The ^1H NMR spectra were registered on a Bruker 500 spectrometer in $CDCl_3$. EA and emission spectra were taken on a SF-103 and Cary 100 spectrophotometers and CM 2203 spectrofluorimeter in organic solvents. Solvents were additionally purified by the known procedures [4]. Water content in the solvents did not exceed 0.02% by Fisher method titration.

ACKNOWLEDGEMENTS

This work was financially supported by the Program of Basic Research of the Preidium of the Russian Academy of Sciences (18-P project-2, 2009), by Analytic Departmental Targeted Program "*Development of the Scientific Potential of Higher School* (2009–2010)" (project no. 2.1.1/827), and Federal Targeted Program "Scientific and Scientific-Pedagogical Potential of Innovative Russia" (2009–2013) (contract no. 02.740.11.0253).

REFERENCES

1. Wood, E. and Thompson, A., *Chem. Rev.*, 2007, vol. 107, p. 1831.
2. Thompson, A. and Dolphin, D., *J. Org. Chem.*, 2000, vol. 65, p. 7870.
3. Marin A. Cato, *New Developments in Organometallic Chemistry Research,* Nova Science Publishers, 2006, p. 63.
4. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.