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# Synthesis, structure and fluorescence of a zinc(II) chelate complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane

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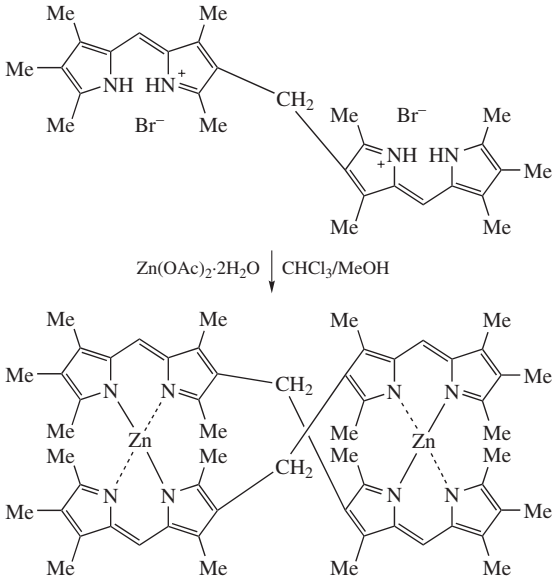
**The crystal structure and spectral properties of new Zn(II) chelate complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)-methane were determined by single-crystal X-ray diffraction, $^1$H NMR, UV and IR spectroscopy; a sufficiently high quantum yield of fluorescence in nonpolar solvents, a long-wavelength emission maximum and good photostability of the complex were demonstrated.**

The materials combining strong luminophoric and chromophoric properties are of interest due to their potential applications in optics. In the past decade, attention has been focused on *p*- and *d*-element complexes with dipyrrolylmethenes and bis(dipyrrolylmethene)s, which often possess intense and controlled fluorescence along with porphyrin-like chromophore characteristics.[1] Currently, fluorophore preparations based on dipyrrolylmethene $BF_2$-complexes are commercially available.[2,3] They can be applied as markers for biomolecules,[4–10] fluorescence switches,[11,12] chemosensors,[13–17] intensity limiters of hard laser radiation,[18] photosensitizers in PDT,[19] intercalators of DNA[20] *etc*.

According to published data,[21–24] the neutral supramolecular complexes of transition metals with 3,3′-bis(dipyrrolylmethene)s can also be used as molecular receptors and photochemical device components. These complexes often exhibit a helical structure, which can be controlled by the modification of a central spacer group and substituents at aromatic rings. According to thermodynamic and spectral studies,[21,25] the methylation of bis(dipyrrolylmethene)s leads to increased stability and improved spectral characteristics of such compounds; thus, the decamethylated bis(dipyrrolylmethene) was chosen as a ligand with potentially useful properties. This work was devoted to the synthesis and structural and spectroscopic characterization of a binuclear zinc(II) complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl) methane.

The synthesis of the bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane ligand as a salt with hydrobromic acid ($H_2L{\cdot}2HBr$) was performed in accordance with a published procedure.[26] The complex of $Zn^{II}$ with this ligand was obtained by a reaction of $H_2L{\cdot}2HBr$ with $Zn(OAc)_2$ (Scheme 1).†




**Scheme 1**

According to X-ray diffraction data‡ the coordination of $Zn^{II}$ to bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane leads to the binuclear complex $[Zn_2L_2]$ containing a double helix formed by the rotation of flat and rigid dipyrrolylmethene fragments around their bonds with the $CH_2$ spacer (Figure 1).

The complex in a crystal occupies a special position on the $C_2$ rotation axis going through C(10) and C(25) atoms. Each Zn atom is linked to four N atoms (two of each ligand). The independent part of a unit cell also contains two molecules of $CH_2Cl_2$. The Zn atom exhibits a skewed tetrahedral coordination: the N–Zn–N angles do not deviate from ideal values of 109.5° by more than 13°. The binuclear complex contained a 16-membered approximately square metallomacrocycle with vertices at Zn(1), Zn(1A), C(10) and C(25) atoms and sides formed by rigid dipyrrolyl-

† Ligand $H_2L{\cdot}2HBr$ (0.18 g, 0.298 mmol) was diluted in 30 ml of chloroform. Triethylamine (0.12 g, 1.16 mmol) was added with stirring and after 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 solution color changed from yellow to red). The mixture was stirred at room temperature for 1 h. Then it was washed with water three times. The chloroform layer was separated, and the solution was evaporated. The precipitate was filtered off, washed with methanol, dried, dissolved in benzene (5 ml) and chromatographed on silica gel (40/100). The eluent was benzene (the first fraction – brilliantly-crimson fluorescence zone); in the second fraction, it was separated by a mixture of benzene and methanol (10:1). The yield: the first zone – 0.225 g, 74.8%. The product was a red-crimson crystal substance with moderate green fluorescence. UV-VIS [$\lambda^{abs}_{max}$/nm ($\varepsilon\times10^{-3}$)]: benzene: 530 (302.6), 478, 369 (CTB); DMF: 525 (219.9), 476, 367 (CTB); $CHCl_3$: 528, 478, 371 (CTB). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$: 1.40 (s, 12H, Me), 1.92 (s, 12H, Me), 2.00 (s, 12H, Me), 2.19 (s, 12H, Me), 2.22 (s, 12H, Me), 3.41 (s, 4H, $CH_2$ spacer), 6.89 (s, 4H, $CH_{meso}$). Found (%): C, 69.01; H, 6.75; N, 11.07. Calc. for $C_{58}H_{68}N_8Zn_2$ (%): C, 69.11; H, 6.80; N, 11.12. The crystals suitable for X-ray diffraction analysis were obtained by slow crystallization from $CH_2Cl_2$–hexane at room temperature.

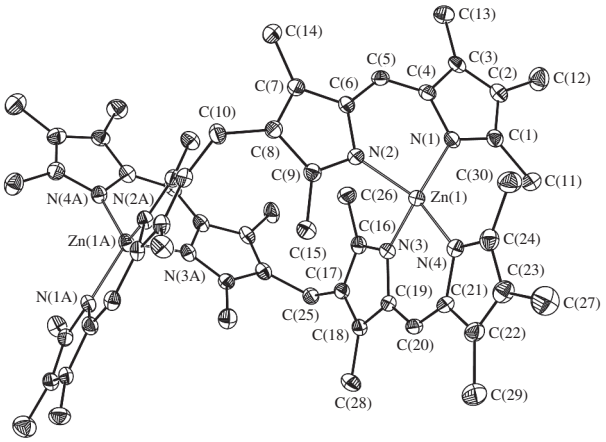



**Figure 1** Molecular structure of $[Zn_2L_2]$ in a crystal. Atoms are represented by thermal ellipsoids ($p$ = 50%). Non-labeled atoms and atoms with 'A' suffix in atom number are symmetry-generated using transformation [–$x$, $y$, 0.5 – $z$]. Hydrogen atoms are omitted for clarity.

methene fragments. The Zn···Zn and C(10)···C(25) distances for this macrocycle are 8.016(3) and 7.856(3) Å, respectively, the Zn(1)···C(10)···Zn(1A) and C(10)···Zn(1)···C(25) angles are 91.1(2)° and 88.8(2)°, respectively. The Zn atom deviates from dipyrrolylmethene planes: the corresponding deviations are 0.234(3) Å for the N(1)–C(4)–C(5)–C(6)–N(2) plane and 0.236(3) Å for the N(3)–C(19)–C(20)–C(21)–N(4) plane. The dihedral angle between these planes is 96.27(9)°, and the deviation of the Zn atom from these planes lowers the distortion of the tetrahedral coordination polyhedron: the angle between the N(1)–Zn(1)–N(2) and N(3)–Zn(1)–N(4) [94.26(9)°] planes is 2° closer to an ideal value of 90°. The Zn–N bond lengths lie in the range of 1.973(2)–1.994(2) Å, which is very close to the value observed in a similar Zn complex

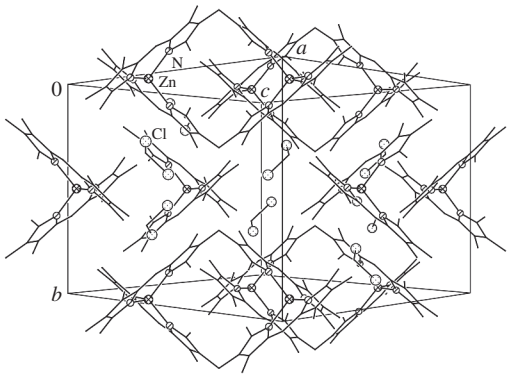



**Figure 2** A fragment of the crystal packing of $[Zn_2L_2]\cdot 4CH_2Cl_2$.

‡ Crystals of $[Zn_2L_2]$ ($C_{58}H_{68}N_8Zn_2\cdot 4CH_2Cl_2$, $M$ = 1347.65) are monoclinic, space group $C2/c$, at 120 K: $a$ = 24.351(6), $b$ = 12.566(4) and $c$ = = 24.130(6) Å, $\beta$ = 119.996(5)°, $V$ = 6395(3) Å$^3$, $Z$ = 4 ($Z'$ = 0.5), $d_{calc}$ = = 1.400 g cm$^{-3}$, $\mu$(MoKα) = 1.130 cm$^{-1}$, $F$(000) = 2800. Intensities of 23519 reflections were measured with a Bruker SMART 1000 CCD diffractometer [$\lambda$(MoKα) = 0.71073 Å, $\omega$-scans, $2\theta < 59°$] and 8853 independent reflections ($R_{int}$ = 0.0984) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the riding model. The refinement converged to $wR_2$ = 0.1075 and GOF = 1.001 for all independent reflections [$R_1$ = = 0.0497 was calculated against $F$ for 4558 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL-Plus 5.0.[27]

CCDC 779451 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

**Table 1** Spectral luminescence characteristics of $[Zn_2L_2]$ complex in organic solvents.

| Solvent | $\lambda^{abs}_{max}$ ($S_0-S_1$)/ nm | $\varepsilon_{max}$ ($S_0-S_1$)/ dm$^3$ mol$^{-1}$ cm$^{-1}$ | $\lambda^{fl}_{max}$, $\lambda_{ex}$ = 495 nm | $\gamma^{fl}$ | $k_{rad}$/ $10^{-8}$ s$^{-1}$ | $\tau_{fl}$/ns |
|---|---|---|---|---|---|---|
| Cyclohexane | 530 | 251800 | 543 | 0.91 | 2.7 | 3.3 |
| Benzene | 530 | 302592 | 545 | 0.56 | 3.2 | 1.7 |
| Hexane | 527 | 294649 | 541 | 0.61 | 3.8 | 1.6 |
| Heptane | 524 | 294105 | 542 | 0.66 | 3.5 | 1.9 |
| Toluene | 531 | 286430 | 545 | 0.64 | 3.2 | 2.0 |
| Chloroform | 529 | 269129 | 544 | 0.025 | 3.4 | 0.074 |
| THF | 528 | 290481 | 542 | 0.13 | 3.4 | 0.38 |
| Ethanol | 525 | 277695 | 542 | 0.005 | 3.7 | 0.013 |
| 1-Propanol | 527 | 250148 | 542 | 0.01 | 3.3 | 0.027 |
| DMF | 526 | 219914 | 543 | 0.002 | 2.8 | 0.007 |

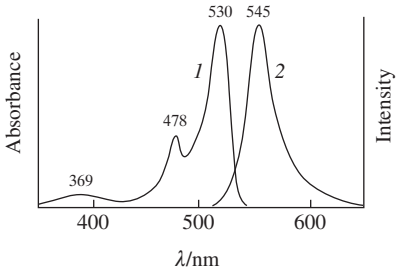



**Figure 3** Electronic (*1*) absorbance and (*2*) emission spectra of $[Zn_2L_2]$ in benzene.

with bis(2,4-dimethyldipyrrin-3-yl)methane [1.962(4)–2.005(4) Å].[1] The crystal lattice of $[Zn_2L_2]\cdot 4CH_2Cl_2$ (Figure 2) is formed mostly by weak H···H, C–H···π and C–H···Cl contacts.

The electronic absorption spectrum of $[Zn_2L_2]$ solutions in organic solvents (Figure 3, Table 1) has a shape typical of such complexes.[1] There is one strong long-wavelength band in the region of 524–531 nm and one less intense band at 475–478 nm. Moreover, a low-intensity wide band corresponding to charge transfer is observed in the region of 360–370 nm. Note that in spite of the absence of a closed macrocyclic system, inherent to porphyrins and metalloporphyrins, the complex of their linear analogue, 3,3′-bis(dipyrrolylmethene), has similar chromophoric properties: the strongest band in the spectra of $[Zn_2L_2]$ and its analogues[1] at 500–550 nm, as well as the most intense band in the typical absorption spectra of metalloporphyrins (the Soret band at 380–400 nm), are characterized by values close to $\varepsilon$ ~ ~ $10^5$ mol$^{-1}$ dm$^3$ cm$^{-1}$. The analysis of quantitative characteristics of electronic absorption spectra of $[Zn_2L_2]$ solutions in various organic solvents§ indicates the existence of a significant solvatochromic effect.

When the complex is transferred from polar electro- and proton-donor solvents (DMF, ethanol, 1-propanol, THF and chloroform) to nonpolar (cyclohexane, benzene, hexane, heptane and toluene), the batochromic shift of the first strong band reaches 7 nm. The spectrum sensitivity to media polarity is due to the solvation of the aromatic chromophore π-system by a nonpolar

§ The electronic absorption spectra of complex solutions in organic solvents (with concentrations of $10^{-5}$–$10^{-6}$ mol dm$^{-3}$) were measured in the region of 300–750 nm on an SF-103 spectrophotometer (Akvilon, Russia) controlled by a PC with the Spectr 1.0 software. The investigations were performed in quartz cells with an optical path length of 10 mm, which were termostated at 298.15 K by Pelt'e cells. Spectral luminescence characteristics and fluorescence quantum yields were measured on an SM2203 spectrometer (Solar, Belarus) using standard techniques. Organic solvents (chemically pure grade) were additionally purified by standard methods.[28] The water content of the solvents, from the results of titrations by Fisher method, was not higher than 0.02%.

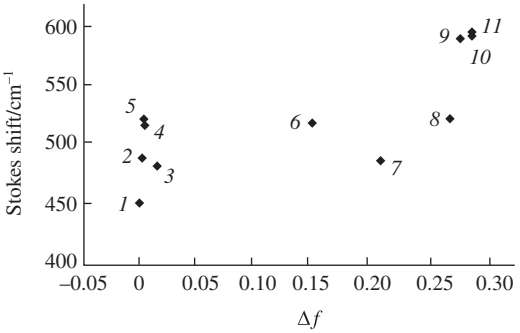



**Figure 4** Dependence of the Stokes shift for $[Zn_2L_2]$ on the function of universal interactions ($\Delta f$) of solvents: (*1*) cyclohexane, (*2*) hexane, (*3*) toluene, (*4*) benzene, (*5*) heptane, (*6*) chloroform, (*7*) tetrahydrofuran, (*8*) 1-propanol, (*9*) dimethylformamide, (*10*) ethanol and (*11*) acetone.

aromatic solvent accompanied by π–π-stacking interactions, which decrease the $^0S$ to $^1S$ energy gap and stabilize the transfer state to result in more long-wavelength absorption.

In contrast to structurally analogous bis(dipyrrolylmethene) $Co^{II}$ and $Ni^{II}$ complexes,[1,29,30] the synthesized $[Zn_2L_2]$ complex demonstrates significant fluorescence. Moreover, $[Zn_2L_2]$ fluorescence is moderate in a solid state and polar solvents, but the fluorescence intensity increases by several orders of magnitude in nonpolar solvents. The first data on the fluorescence properties of $[Zn_2L_2]$ in organic solvents (Figure 3, Table 1) show that the emission spectrum is nearly a mirror reflection of the absorption spectrum with a higher Stokes shift (15 nm): the intense band maximum is observed at 541–545 nm. The $[Zn_2L_2]$ complex exhibits intense fluorescence with a quantum yield close to unity in nonpolar and weakly polar saturated and aromatic hydrocarbons (cyclohexane, benzene, hexane, heptane and toluene). In polar solvents (DMF, EtOH, PrOH and $CHCl_3$) the fluorescence efficiency of $[Zn_2L_2]$ is up to ~450 times lower than that in nonpolar solvents and approaches zero in acetonitrile. This means that, in ethanol and other polar solvents, for which the radiation constant is not smaller than in nonpolar solvents (Table 1), the probability of nonradiative deactivation of the excited state is large, which is determined by specific interactions in the solvation shell (Figure 4). It should be noted that various solvents only slightly affect the positions of bands; however, the radiation quantum yield decreases by orders of magnitude upon transfer from nonpolar solvents to polar ones, such as proton- and electron-donor alcohols, chloroform, DMF, *etc.* (Table 1). Increasing the solvent polarity violates series with respect to the position and intensity of absorption bands, especially, with respect to fluorescence quantum yields (Table 1). This implies a specific character of interactions in certain solvents and is confirmed by the violation of the linear dependence of the Stokes shift on the function of universal interactions for proton-donor (electron-acceptor) and proton-acceptor (electron-donor) solvents [points (*6*)–(*11*) in Figure 4]. The radiation constant depends weakly on the solvent; however, the solvation shell formed by the solvent plays a significant role in the deactivation of the excitation energy.

The sufficiently high fluorescence quantum yield (comparable with that of $BF_2$-dipyrrolylmethene complexes) in nonpolar solvents,[31] long-wavelength emission maximum and good photostability (the complexes were stable for longer than a year in the light) demonstrate the possibility of potential usage of such a complex not only as a fluorescence marker but also as a sensor of medium polarity, protein surfaces, biomembranes *etc*.

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