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Synthesis, structure and optical properties of a Co^{II} complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane

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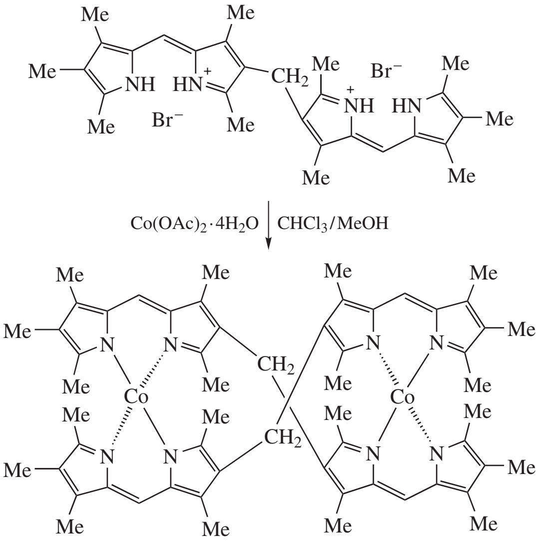
The self-assembly of bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane with Co^{II} gives the binuclear dimeric helicate [Co$_2$L$_2$], whose structure was characterized by X-ray diffraction analysis.

Polybipyridine ligands are particularly interesting with respect to their ability to generate helicates,[1] grids,[2] cages,[3] ladders[4] and rings.[5] In contrast to bipyridine, dipyrrolylmethenes are ideal building blocks for supramolecular self-assembly. Dipyrrolylmethenes consisting of two pyrroles are typical π-conjugated bidentate monoanionic ligands for metal ions in natural and artificial systems. Therefore, they are promising scaffoldings for self-assemblies[6–8] to give neutral coordination oligomers. By varying bridge spacers between two dipyrrin units, the self-assembly of corresponding bis(dipyrrolylmethene) ligands with metal ions give supramolecules with different geometric shapes.[7,9,10] This work was devoted to the synthesis, crystal structure and spectral properties of the Co^{II} complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane [Co$_2$L$_2$]. The ligand as a salt of hydrobromic acid (H$_2$L·2HBr) was synthesized in accordance with a published procedure.[11] The complex of Co^{II} with this ligand was obtained by a reaction of H$_2$L·2HBr with Co(OAc)$_2$ (Scheme 1).[†]

The complex [Co$_2$L$_2$] occupies a special position on the C_2 rotation axis going through the C(11) and C(26) atoms and contains two L molecules in which flat and rigid dipyrrolylmethene fragments rotate around their bonds with the CH$_2$ spacers [C(11) and C(26) atoms] (Figure 1). The dihedral angles between the N(1)–C(1)···C(9)–N(2) and N(1A)–C(1A)···C(9A)–N(2A) (L1) and N(3)–C(16)···C(24)–N(4) and N(3A)–C(16A)···C(24A)–N(4A) (L2) planes are 97.8 and 78.5°, respectively.[‡]

The Co atom is linked to four N atoms (two of each ligand L) with the distorted tetrahedron geometry of coordination units. The Co–N bond lengths [1.978(3)–1.991(3) Å] lie in a range very close to the value observed in a similar Co complex with



Scheme 1

[†] Ligand H$_2$L·2HBr (0.1 g, 0.166 mmol) was dissolved in 10 ml of chloroform. Triethylamine (0.12 g, 1.16 mmol) was added with stirring, and a solution of Co(AcO)$_2$·4H$_2$O (0.207 g, 0.83 mmol) in 10 ml of methanol was added after 3 min. The mixture was stirred for 1 h. Then, the chloroform fraction was washed with water to remove excess salt, methanol and triethylamine. The chloroform layer was separated, evaporated and chromatographated on silica gel (40/100). The eluent was benzene. Then, the solvent was removed, and the complex was precipitated by methanol. The product was separated as green powder with metallic luster. Yield, 0.045 g (54.2%). ^{1}H NMR (CDCl$_3$) δ: 2.01 (s, 12 H, Me), 2.15 (s, 12 H, Me), 2.27 (s, 12 H, Me), 2.56 (s, 12 H, Me), 2.65 (s, 12 H, Me), 3.58 (s, 4 H, CH$_2$ spacer), 6.24 (s, 2 H, CH$_{meso}$), 6.32 (s, 2 H, CH$_{meso}$). IR (KBr, ν/cm^{-1}): 2908, 2854, 1593, 1437, 1391, 1363, 1221, 1164, 1101, 1043, 943, 917, 845, 785, 739, 670. MS, m/z: 996.10 [M + H]$^+$, 1013.13 [M + NH$_4$]$^+$. Found (%): C, 69.91; H, 6.78; N, 11.17. Calc. for C$_{58}$H$_{68}$N$_8$Co$_2$ (%): C, 70.01; H, 6.89; N, 11.26.

[‡] Crystals of [Co$_2$L$_2$] suitable for X-ray analysis were grown by slow diffusion of hexane into dichloromethane solutions of the complexes.

Crystal data. C$_{58}$H$_{68}$N$_8$Co$_2$·1.5MeOH, M = 1041.11, monoclinic, space group $C2/c$, at 100 K: a = 11.5933(15), b = 24.341(3) and c = 22.448(3) Å, β = 92.813(3)°, V = 6327.1(14) Å^3, Z = 4 (Z' = 0.5), d_{calc} = 1.093 g cm^{-3}, μ(MoKα) = 0.566 mm^{-1}, F(000) = 2204. Intensities of 9810 reflections were measured with a Bruker SMART 1000 CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta < 52°$] and 6139 independent reflections (R_{int} = 0.0470) 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 with $U(\mathrm{H}) = nU(C)$, n = 1.5 for methyl groups and n = 1.2 for other moieties. In structure, there are two large voids occupied by the disordered solvent (MeOH) molecules, which cannot be localized. The unit cell contains six methanol molecules, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. All atoms of methanol molecules were not located. However, these atoms were included in the empirical formula and moiety formula. The refinement converged to wR_2 = 0.1440 and GOF = 1.005 for all 6139 independent reflections [R_1 = 0.0599 was calculated against F for 3720 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL-Plus 5.0.

CCDC 948340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2014.

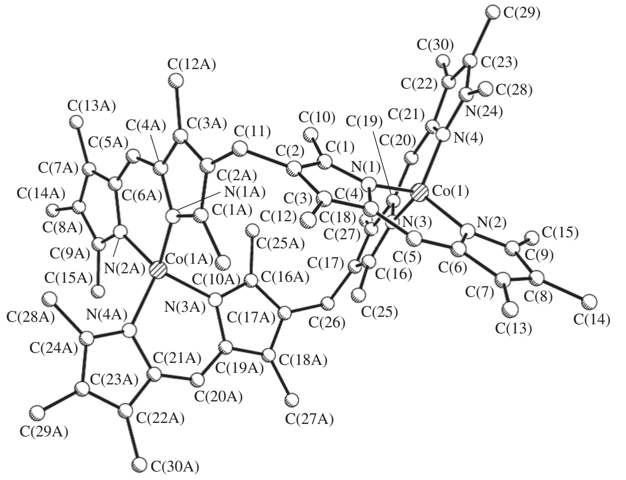


Figure 1 Molecular structure of $[Co_2L_2]$ in a crystal. Atoms are represented by thermal ellipsoids (p = 50%). Non-labeled atoms and atoms with 'A' suffix in atom numbers are symmetry-generated using transformation ($-x$, y, $0.5 - z$). Hydrogen atoms are omitted for clarity.

bis(2,4,8,10-tetramethyl-9-methoxycarbonylethyldipyrrin-3-yl)-methane [1.964(5)–1.985(4) Å].[12] The Co atom deviates from dipyrrolylmethene planes: the corresponding deviations are 0.119(4) Å for the N(1)–C(1)···C(9)–N(2) plane and 0.049(3) Å for the N(3)–C(16)···C(24)–N(4) plane, the dihedral angle between these planes is 86.20(6)°. The tetrahedron distortion is small, the angle between the N(1)–Co(1)–N(2) and N(3)–Co(1)–N(4) [86.8(1)°] planes is 3.2° closer to an ideal value of 90°.

The three-dimensional architecture of the molecule with the approximate structure of a 16-membered square with vertices at the Co(1), Co(1A), C(11) and C(26) atoms and sides is formed by rigid dipyrrolylmethene fragments (Figure 2). The Co···Co and C(11)···C(26) distances for this macrocycle are 7.712(3) and 8.098(3) Å, respectively; the dihedral angles between N(1)–C(1)···C(9)–N(2)/N(3A)–C(16A)···C(24A)–N(4A) and N(1A)–C(1A)···C(9A)–N(2A)/N(3)–C(16)···C(24)–N(4) planes are 138.7 and 41.3°, respectively.

The complex structure also contains disordered 1.5 MeOH molecules which occupy space between the $[Co_2L_2]$ molecules (Figure 3). In spite of methanol molecules were not located, the positions of the cavities occupied by MeOH are found (they are marked by large circles).

The UV-VIS data for $[Co_2L_2]$ in different solvents are summarized in Table 1. Binuclear double stranded helicate $[Co_2L_2]$ containing four dipyrrolylmethene units is a strong chromophore. The electronic absorption spectra[§] of the complex exhibit one strong long-wavelength (lgε is 5.09) band at 526–530 nm and one less intense band at 492–495 nm. Moreover, a low-intensity wide band is observed at 376–377 nm. This type of spectrum is characteristic of the previously synthesized complexes of Co^{II} with other bis(dipyrrolylmethenes).[12] In the electronic absorption spectra, the first, second and third bands are assigned to the $^0S \rightarrow {}^1S$, $^0S \rightarrow {}^2S$ and $^0S \rightarrow {}^3S$ electronic transitions, respectively. The analysis of the electronic absorption spectra of $[Co_2L_2]$ solutions in various organic solvents indicates the existence of a solvatochromic effect. When the complex is transferred from polar electron- and proton-donor solvents (DMF and chloroform) to nonpolar ones (cyclohexane and benzene), the bathochromic shift of the first strong band reaches 4 nm. The red shift of the first band maximum in aromatic benzene can be attributed to π–π-stacking interactions of the aromatic π-systems of the chromophores and solvents, which decrease ^0S to ^1S energy gap and stabilized the transition state to result in more long-wavelength absorption. Importantly, in contrast to the bis(dipyrrolylmethenates) of zinc(II), cadmium(II) and mercury(II)[14–17] the helicate $[Co_2L_2]$ is not a fluorophore.

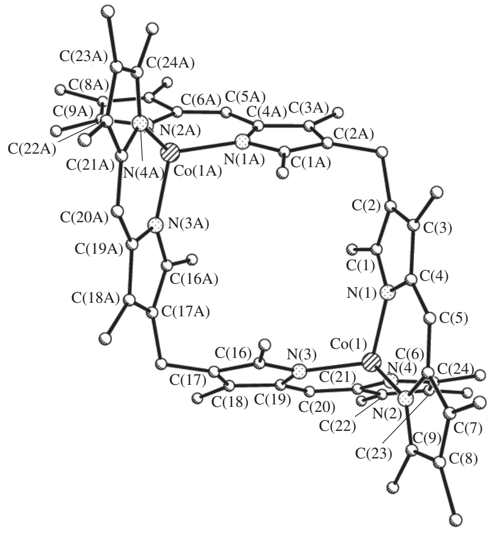


Figure 2 Structure of a 16-membered approximately square core in $[Co_2L_2]$.

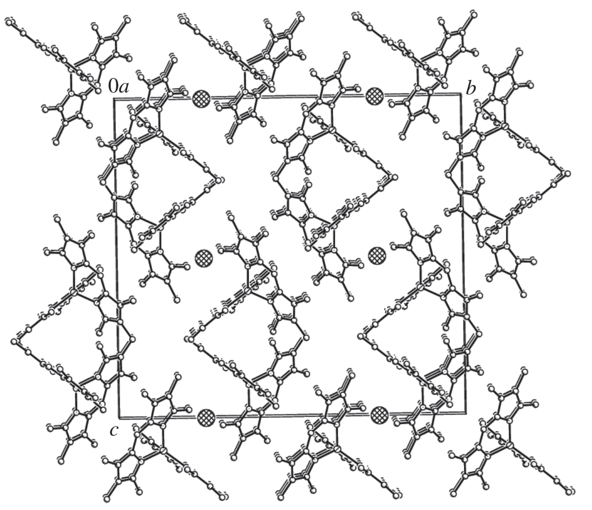


Figure 3 Crystal packing in structure $[Co_2L_2]$.

Table 1 Spectral characteristics of $[Co_2L_2]$ in organic solvents.

Solvent	$\lambda_{\max}^{\text{abs}}$/nm (lg$\varepsilon$)
Cyclohexane	529, 492, 376
Benzene	530 (5.08), 495 (4.75), 377 (4.30)
Chloroform	528 (5.08), 494 (4.77), 377 (4.32)
DMF	526 (5.09), 494 (4.76), 377 (4.32)

The Co^{II} assisted self-assembly of a bis(dipyrrin-3-yl)methane ligand gives binuclear double stranded helicate, in which, each Co^{II} center is coordinated to two N atoms of each ligand forming the distorted tetrahedron geometry.

[§] The electronic absorption spectra of complex solutions in organic solvents (with concentrations of 10^{-6}–10^{-5} mol dm^{-3}) were measured in the 350–650 nm region on an SF-103 spectrophotometer (Akvilon, Russia) controlled by a PC with the Spectr 1.0 software. The measurements were performed in quartz curvettes with an optical path length of 10 mm, which were thermostated at 298.15 K. The IR spectra were recorded on an Avatar 360FT-IR ESP spectrophotometer in tablets with KBr. The ^{1}H NMR spectra were measured on a Bruker 200 ^{1}H NMR spectrometer in CDCl$_3$ solutions. Organic solvents (chemically pure grade) were additionally purified by standard methods.[13] The water content of the solvents was no higher than 0.02%, based on the results of titrations by the Fischer method.

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References

1 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.

2 I. Weissbuch, S. Cohen, H. Cohen, L. Leiserowitz, M. Lahav, K. Kjaer, P. B. Howes, J. Als-Nielsen, J.-M. Lehn, P. N. W. Baxter, G. S. Hanan and U. S. Schubert, *J. Am. Chem. Soc.*, 1998, **120**, 4850.

3 M. Fujita, S. Y. Su, T. Kusukawa, H. Funaki, K. Ogura and K. Yamaguchi, *Angew. Chem. Int. Ed.*, 1998, **37**, 2082.

4 P. N. Baxter, G. S. Hanan and J.-M. Lehn, *Chem. Commun.*, 1996, 2019.

5 S. A. Baudron, *Cryst. Eng. Comm.*, 2010, **12**, 2288.

6 S. R. Halper and S. M. Cohen, *Chem. Eur. J.*, 2003, **9**, 4661.

7 H. Maeda, *J. Incl. Phenom. Macrocycl. Chem.*, 2009, **64**, 193.

8 A. Thompson, S. J. Rettig and D. Dolphin, *Chem. Commun.*, 1999, 631.

9 E. Wood and A. Thompson, *Chem. Rev.*, 2007, **107**, 1831.

10 L. Ma, J.-Y. Shin, B. O. Patrick and D. Dolphin, *Cryst. Eng. Comm.*, 2008, **10**, 1539.

11 G. B. Guseva, N. A. Dudina, E. V. Antina, A. I. V'ugin and A. S. Semeikin, *Russ. J. Gen. Chem.*, 2008, **78**, 1215 (*Zh. Obshch. Khim.*, 2008, **78**, 987).

12 L. Yang, Y. Zhang, G. Yang, Q. Chen and J. S. Ma, *Dyes and Pigments*, 2004, **62**, 27.

13 A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publishers, Inc., New York, 1955.

14 E. V. Antina, M. B. Berezin, N. A. Dudina, G. B. Guseva, L. A. Antina and A. I. V'yugin, *Russ. J. Gen. Chem.*, 2010, **80**, 1216 (*Zh. Obshch. Khim.*, 2010, **80**, 1048).

15 M. B. Berezin, E. V. Antina, N. A. Dudina, I. S. Bushmarinov, M. Yu. Antipin, L. A. Antina and G. B. Guseva, *Mendeleev Commun.*, 2011, **21**, 168.

16 L. A. Antina, N. A. Dudina, M. B. Berezin, G. B. Guseva and E. V. Antina, *Russ. J. Gen. Chem.*, 2011, **81**, 591 (*Zh. Obshch. Khim.*, 2011, **81**, 496).

17 L. A. Antina, G. B. Guseva, A. I. V'yugin and E. V. Antina, *Zh. Koord. Khim.*, 2012, **38**, 529 (in Russian).

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