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An efficient one-pot route to an aza-bridged bis-phenanthroline macrocyclic compound

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Abstract

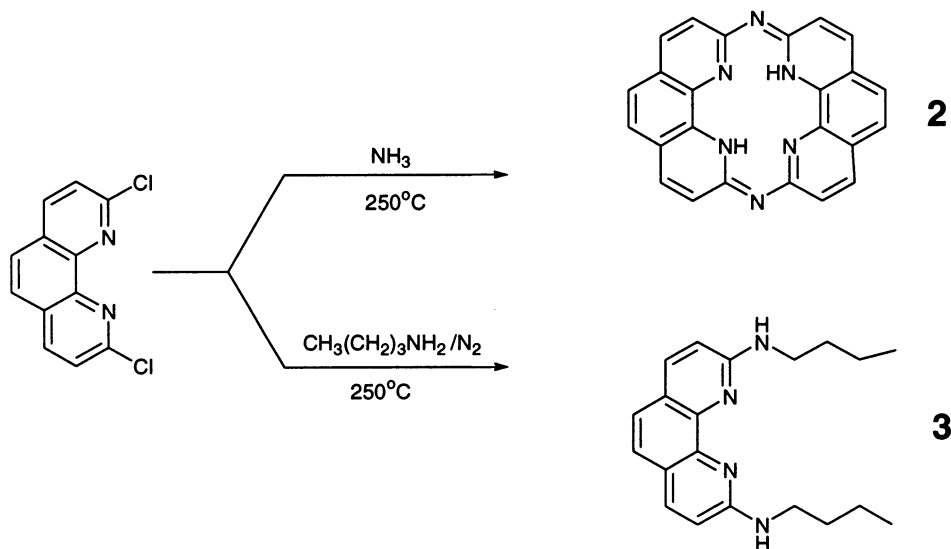
A facile synthesis of an aza-bridged bis-1,10-phenanthroline macrocycle is described. X-ray crystallographic analysis of the aza-bridged bis-1,10-phenanthroline revealed that the two central hydrogen atoms were localized on two of the opposite central nitrogen atoms similar to those of free base porphyrins. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: aza compounds; macrocycles; polyazacyclophanes.

1,10-Phenanthroline, a versatile ligand, is the parent of an important class of chelating ligands. Compared to the more common 2,2'-bipyridine system, 1,10-phenanthroline can form complexes with metal ions more rapidly. Another consequence of the planar structure of 1,10-phenanthroline is its ability to participate as an intercalating or groove-binding species with DNA or RNA. One other important property of the 1,10-phenanthroline nucleus is its ability to act as a triplet-state photosensitizer. Transition metal complexes of these ligands have been extensively investigated because of their photochemical,¹ electrochemical² and biological properties.³

Bridged bis-phenanthroline macrocyclic compounds are of interest owing to their potential applications in the catalytic reduction of CO₂ and as probes for DNA etc.^{4,5} Preparation of the aza-bridged bis-phenanthroline macrocycle H₂HAPP (**2**) was first reported by Ogawa⁶ et al. Since then many studies on this ligand and its metal complexes have been carried out.⁷ Owing to the low yields and the problems associated with purification caused by poor solubility of these phenanthroline cyclophanes, little attention has been paid to them recently. In this communication, we wish to report a facile method for the preparation of H₂HAPP by direct reaction of 2,9-dichloro-1,10-phenanthroline (**1**) with NH₃, as well as the single crystal structure of this ligand (Scheme 1).

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Scheme 1.

H₂HAPP was synthesized by the following procedure: 2,9-dichloro-1,10-phenanthroline (1) (1.1 g), prepared by a known method,³ was placed in a flask which was heated to 200°C (oil-bath). Ammonia gas was introduced and the temperature raised to 250°C for 8 hours. The yellow–orange mixture was washed with CH₂Cl₂ and CH₃OH, respectively, several times and dried in vacuo to furnish H₂HAPP·2HCl (0.83 g, yield: ~84%).⁸ We found that when the temperature was raised to 300°C, the product was H₂HAPP.⁹ Its ¹H NMR (d-TFA) spectrum was the same as that of H₂HAPP·2HCl. We also tried to introduce butylamine to the reaction system in a stream of N₂ gas, but failed to obtain the corresponding macrocyclic compound. Only 2,9-dibutylamino-1,10-phenanthroline (3) (yield: ~85%) was obtained.

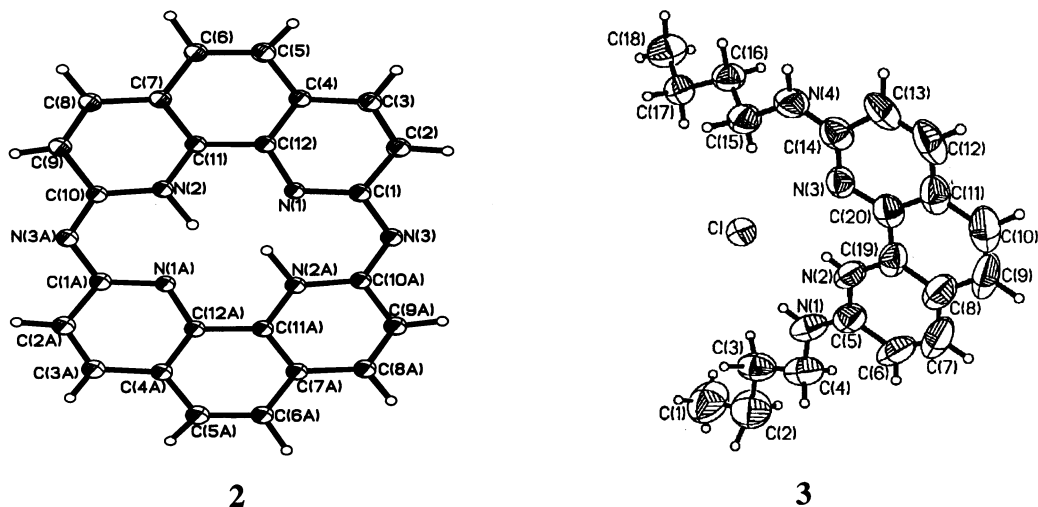


Figure 1. ORTEP drawings of 2 and 3 with the atom numbering

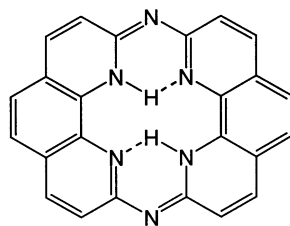


Figure 2. Structure of H₂HAPP

We obtained a single crystal of **2** by direct sublimation from the reaction vessel, and a single crystal of **3** was grown in dichloromethane at 4°C. The ORTEP¹⁰ representations of **2** and **3** with atomic numbering are given in Fig. 1.¹¹ Macrocyclic **2** is a planar structure, contrary to the results reported by Ogawa.¹² The crystal structure analysis revealed that its two central hydrogen atoms are localized on two of the opposite central nitrogen atoms similar to those of free base porphyrin. Although there is no significant difference for the C–N bond distances of the two different inner nitrogen atoms,¹³ the C–N–C angle of the protonated N atom (124.7(4)°) is larger than that of nonprotonated one (119.3(4)°). This angle difference is in agreement with similar structures reported.¹⁴ The C–N–H angles (C(10)–N(2)–H(2N), 115°; C(11)–N(2)–H(2N), 120°) around the protonated N atom are not symmetrical, which indicates hydrogen bonding between H(2N) and N(1A). This is also supported by the short H(2N)⋯N(1A) distance (1.786 Å). For the outer nitrogen atom, the C–N bond distances are different and higher C–N bond order is observed when it is closer to the protonated N atom.¹⁵

We calculated the C–C π -bond order of H₂HAPP by use of a semi-empirical equation,¹⁶ the results suggest H₂HAPP possesses a structure as shown in Fig. 2.

In conclusion, we have developed a convenient and efficient method to prepare an aza-bridged bis-phenanthroline macrocycle, and have verified that the two central hydrogen atoms of H₂HAPP are localized on two of the opposite central nitrogen atoms by using X-ray crystal structure analysis.

Acknowledgements

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References

1. Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.
2. Kelly, D. M.; Vos, J. G. In *Electroactive Polymer Electrochemistry Part2*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1994; pp. 173–232.
3. Sammes, P. G.; Yahioğlu, G. *Chem. Soc. Rev.* **1994**, 327–334.
4. (a) Costamagna, J.; Canales, J.; Vargas, J.; Ferraudi, G. *Pure Appl. Chem.* **1995**, *67*, 1045–1052. (b) Costamagna, J.; Ferraudi, G.; Cnanales, J.; Vargas, J. *Coord. Chem. Rev.* **1996**, *148*, 221–248 and references cited therein.

5. (a) Cheng, C.-C.; Kuo, Y.-N.; Chuang, K.-S.; Luo, C.-F.; Wang, W.-J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1255–1257. (b) Hirai, M.; Shinozuka, K.; Sawai, H.; Ogawa, S. *Chem. Lett.* **1992**, 2023–2026.
6. (a) Ogawa, S.; Yamaguchi, T.; Gotoh, N. *J. Chem. Soc., Chem. Commun.* **1972**, 577–578. (b) Ogawa, S.; Yamaguchi, T.; Gotoh, N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 976–978.
7. (a) Wang, W.-J.; Yu, T.-M. *Synth. Metals* **1989**, *29*, F145–150. (b) Wang, W.-J.; Liao, I.-S. *Synth. Metals* **1993**, *55*, 1962–1967. (c) Cotamagna, J.; Canales, J.; Vargas, J.; Alvarado, A.; Ferraudi, G. *J. Ind. Chem.* **1993**, *70*, 877–883. (d) Costamagna, J.; Canales, J.; Vargas, J.; Camalli, M.; Caruso, F.; Rivarola, E. *Pure Appl. Chem.* **1993**, *65*, 1521–1526. (e) Vargas, J.; Ferraudi, G.; Canale, J.; Costamagna, J. *Inorg. Chim. Acta* **1994**, *226*, 151–157.
8. Anal. for H₂HAPP·2HCl (C₂₄N₆H₁₆Cl₂), found (calcd): C, 61.50 (62.74); H, 3.88 (3.49); N, 17.89 (18.30)%. ¹H NMR (d-TFA) δ (ppm): 8.02 (4H, d, *J*=9.0 Hz), 8.27 (4H, s), 8.93 (4H, d, *J*=9.0 Hz). FAB-MS (M+1)/z: 387; IR: 3007, 2768, 1652, 1604, 1578, 1501, 1482, 1470, 1440, 1410, 1362, 1342, 1308, 1260, 1226, 1201, 1144, 1094, 984, 913, 850, 802, 732, 698, 642, 598, 579, 467 cm⁻¹.
9. Anal. for H₂HAPP·H₂O (C₂₄N₆H₁₆O), found (calcd): C, 71.84 (71.28); H, 3.86 (3.47); N, 20.78 (20.79)%. IR: 3025, 2762, 1642, 1582, 1559, 1531, 1503, 1440, 1420, 1383, 1342, 1317, 1262, 1221, 1198, 1150, 1088, 988, 967, 894, 843, 793, 732, 697, 644, 616, 588, 523, 470 cm⁻¹.
10. Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
11. **Crystallographic data and data collection parameters:** H₂HAPP (**2**), C₂₄H₁₄N₆, *M*=386; crystal size: 0.40×0.30×0.15 mm, monoclinic, space group *P*2₁/*c*, *a*=4.420(1), *b*=9.988(2), *c*=19.008(3) Å, β=95.47(2)°, *V*=835.3(3) Å³, *Z*=2, *D*_c=1.536 g cm⁻³, μ(Mo-Kα)=0.096 mm⁻¹, *F*(000)=400, *T*=298 K. 1669 reflections were measured (1465 unique, *R*_{int}=0.0596) on a Siemens P4 diffractometer in the range 1.50<θ<25.00°, 0<*h*<5, 0<*k*<11, -22<*l*<22, operating in ω scan mode and using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Semi-empirical absorption correction via φ scans was applied. **Structure solution and refinement:** The structure was solved by the direct method and refined anisotropically based on *F*² by full-matrix least-squares techniques using the SHELXTL (Ver 5.10) program. All hydrogen atoms were located by Fourier synthesis and refined isotropically without any constraints or restraints. The final refinement gave *R*₁=0.0663, *wR*₂=0.1226. The final difference map showed peaks between 0.216 and -0.231 e Å⁻³.
12. Seno, M.; Tsuchiya, S.; Ogawa, S. *J. Am. Chem. Soc.* **1977**, *99*, 3014–3018.
13. Nishigaki, S.; Yoshioka, H.; Nakatsu, K. *Acta Crystallogr., Sect. B* **1978**, *34*, 875.
14. Hensen, K.; Kettner, M.; Bolte, M. *Acta Crystallogr., Sect. C* **1998**, *54*, 359–361.
15. Ansell, C. W. G.; Lewis, J.; Raithby, P. R.; Ramsden, J. N.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1982**, 546.
16. Cruickshank, D. W. J. *Tetrahedron* **1962**, *17*, 155.