636 **RESEARCH PAPER** SEPTEMBER, 636–637 JOURNAL OF CHEMICAL RESEARCH 2004

Self-assembly of 1,4-bis(pyrrol-2-ylmethyleneamine)butane mediated by Ni(II) and weak intermolecular interactions

Lanying Yang[a], Xufeng Shan[a], Qingqi Chen[b] and Jin Shi Ma[a,*]

[a]CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

[b]BioMarin Pharmaceutical, Inc., 46 Galli Drive, Novato, CA 94949, USA

A complex [NiL] was prepared by the self-assembly of 1,4-bis(pyrrol-2-ylmethyleneamine)butane (H_2L) with $Ni(OAc)_2{\cdot}2H_2O$, its structure was elucidated by X-ray analysis and the weak intermolecular interactions play a crucial role in the molecular packing.

Keywords: crystal structure, 1,4-bis(pyrrol-2-ylmethyleneamine)butane, weak interaction

---

The ligand, a pyrrol-2-yl Schiff base or pyrrol-2-ylmethyleneamine, and its metal complexes have been long known.[1] Macrocycles containing pyrrol-2-yl-methyleneamine units, such as texaphyrins and expanded porphyrins,[2] have been extensively investigated. The reaction of simply pyrrol-2-ylmethyleneamine ligands with divalent metal ions was known to give mononuclear dimeric complexes.[1] Several linear spacer bridged bis(pyrrol-2-ylmethyleneamine)s and their complexes with metal ions were recently reported,[3] which demonstrated that both the preparation of ligands and the complexes were highly efficient. Furthermore, the metal complexes formed by pyrrol-2-ylmethyleneamines were neutral molecules and possessed good solubility in common solvents. Those properties attract us to further explore their application as a building block for supramolecular self-assembly study. By varying the bridging spacer between two pyrrol-2-ylmethyleneamine units, our group has recently synthesised mono-stranded,[4-6] double-stranded helicates,[5] trimeric triangles,[6] tetrameric squares[6] and 1D, 2D and 3D networks formed through self-assembly of the corresponding ligands with Cu(II) and Ag(I).[5,7]

In a very recent work, Carcelli and coworkers reported the synthesis of complexes of ethylene and propylene bridged bis(pyrrol-2-ylmethyleneamine) ligands with Ni(II).[3f] In this paper, we report the X-ray structural characterisation of the complex of 1,4-bis(pyrrol-2-ylmethyleneamine)butane with Ni(II) and the weak intermolecular interactions which play a crucial role in the molecular packing. The weak intermolecular interactions in Ni(II) complexes are rarely reported in the literatures.

The molecular ion peak (*m/z*) of the complex observed in the FAB–MS is 299 $[M+H]^+$, which is assigned to the corresponding mononuclear monomeric complex with a ligand to metal ratio of 1:1. It is a neutral species resulting from the deprotonation of the NH group of the pyrrole rings. The 1,4-bis(pyrrol-2-ylmethyleneamine)butane acts as tetradentate ligand and the four N atoms coordinate to the same Ni centre. The Ni(II) is four-coordinated by four nitrogen atoms of the ligand forming a NiN_4 core, which adopts a distorted square-planar conformation (Fig. 1a). The Ni–N bond lengths range from 1.886(3) to 1.940(4) Å. The Ni(II) centre deviates by 0.0658 Å from the plane defined by N(1), N(2), N(1A) and N(2A). The sum of the bond angles [$\angle$ N(1)–Ni–N(2) = 83.1(2)°, $\angle$ N(2)–Ni–N(3) = 98.1(2)°, $\angle$ N(3)–Ni–N(4) = 83.7(2)° and $\angle$ N(4)–Ni–N(1) = 96.9(2)°] is 361.8°, being very close to 360°. The dihedral angles, defined by the intersection of two pyrrol-2-ylmethyleneamine planes at the nickel center is 17.1°, indicating the deviation from the square-planar coordination geometry. Interestingly, the complex crystallised in the solid state as enantiomers pairs of right- (P) and left-handed (M) helices [8] (Fig. 1b), and they are arranged alternately in the crystal (Fig. 1c).

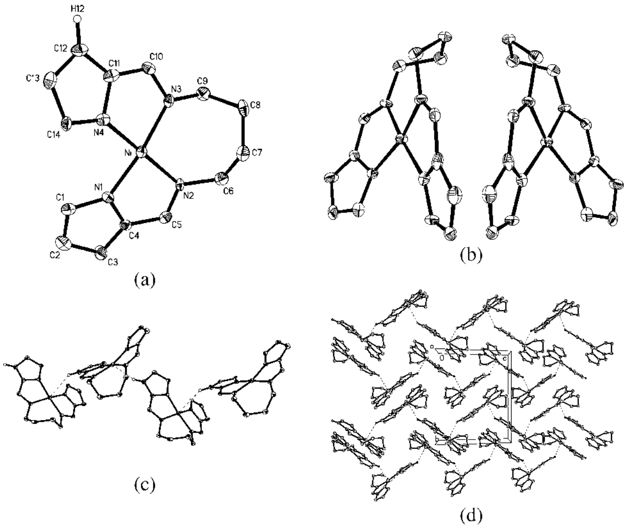

Fig. 1 (a) The ORTEP structure of the Ni(II) complex with atom labelling. (b) The enantionmeric pairs for the complex. (c) The C–H···Ni weak intermolecular hydrogen bonding in the crystal of the complex. (d) The packing diagram of the Ni(II) complex showing the 1D zigzag chain via C–H···Ni interactions.

The weak intermolecular hydrogen bonding between Ni···H(12)–C(12) is found in the crystal of the complex and plays a crucial role in the formation of 1D zigzag chains in the crystal of the complex, in which the enantionmeric pairs of the complex are arranged alternately (Figs 1c and 1d). The distances of Ni···H and Ni···C are 2.819 and 3.639 Å respectively, and the C–H···Ni angle is 147.6°. In this neutral compound the "short" (C)H···Ni separation associated with large C–H···Ni angle most likely correspond to C–H···Ni hydrogen bonds.[9] Although the regular weak hydrogen bonds are very common in chemical and biological systems,[5,10] these noncovalent interactions may have important consequences on the solid-state structure of organometallic molecules and on the chemical and physical properties of the solid materials.[9b]

Experimental

Melting point was determined on a Yanaco MP-500 micro-melting point apparatus and uncorrected. NMR spectra were recorded on a Bruker Avance dpx 400MHz instrument using TMS as an internal standard. Mass spectra were obtained on a KYKY-ZHP-5 spectrometers. IR spectra were recorded on a Tensor 27 spectrometer, and Raman spectra were recorded on a RFS 100 spectrometer. Elemental analyses were performed on a Carlo Erba-120 elemental analyser.

Syntheses of 1,4-Bis(pyrrol-2-ylmethyleneamine)butane Ni (II) complex: A solution of $Ni(OAc)_2{\cdot}2H_2O$(1 mmol) in methanol (20 ml) was added to a solution of 1,4-bis(pyrrol-2-ylmethyleneamine)butane[5] (1 mmol) in methanol (10 ml) with stirring. After 10min a solution of

---

* Correspondence. E-mail: isma@iccas.ac.cn

KOH (2 mmol in 30ml methanol) was added. The mixture was then stirred for another 30min. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered to remove any insoluble materials. The filtrate was concentrated under vacuum to dryness, and crystallised in CH_2Cl_2–MeOH to give the expected products as orange-red crystals. Yield: 95%; m.p. 158–160˚C; ^{1}H NMR (400 MHz, $CDCl_3$, 25˚C, TMS): δ = 1.87 (s, 4H; CH_2); 3.60 (s, 4H; CH_2); 6.14 (dd, J = 3, 3 Hz, 2H, pyrrole-H_4), 6.58 (d, J = 3 Hz, 2H; pyrrole-H_3), 6.78 (m, 2H; pyrrole-H_5), 7.15 (s, 2H; imine-H) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): δ = 26.2, 54.3, 112.0, 115.7, 137.6, 139.9, 161.1 ppm. FAB-MS: (m/z, %): 299 ($M+H^+$, 18). FT-IR data (KBr pellet, cm^{-1}): 3091(w), 2928(m), 2857(w), 1597(s), 1442(m), 1369(m), 1037(s), 738(s). Raman data (cm^{-1}): 3090(m), 2929(m), 2859(w), 1591(s), 1267(m); UV-Vis (CH_2Cl_2): λ_{max} (ε) = 316 nm (23 600). Anal. Calcd for $C_{14}H_{16}N_4Ni$: C, 56.24; H, 5.39; N, 18.74. Found: C, 55.97; H, 5.29; N, 18.68.

Crystal data: $C_{14}H_{16}N_4Ni$, Mr = 299.00, Monoclinic, $P2_1/c$, a = 10.2207(4) Å, b = 12.5629(5) Å, c = 11.2953(5) Å. V = 1319.21(9) Å^3, D_c = 1.506 g cm^{-3}, Z = 4, μ = 1.461 cm-1, T = 293(2)K. A dark red crystal with dimensions of 0.29 mm × 0.20 mm × 0.04 mm was mounted on a Rigarku Raxis Rapid IP diffractometer equipped with a graphite monochromator for data collection. The determination of unit cell parameters and data collections were performed with Mo$K\alpha$ radiation (λ = 0.71073 Å). A total of 5630 reflections with 3014 independent ones with R_{int} = 0.1283 and 1121 observed reflections with $I > 2\sigma(I)$ were collected in the range of $2.56 < \theta < 27.47$ ˚ by an ω/θ scan mode at 293(2) K. All data were corrected by using PSI scan method. The structure was solved by direct methods with SHELXL-97 program. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. Ni(II) atom in the complex was located from E-maps. The hydrogen atoms were added theoretically, riding on the concerned atoms and being refined with fixed thermal factors. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to the final R = 0.0658 and wR = 0.0822. S = 0.703. Molecular graphics were drawn with the program package XP. Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition number CCDC-209254.

This work was financially supported by NSFC (50221201) and the major state basic research development program (G2000078100) of China.

Received 2 June 2004; accepted 3 August 2004
Paper 04/2553

References

1 (a) A. Chakravorty and R.H. Holm, *Inorg. Chem.*, 1964, **3**, 1521; (b) J.H. Weber, *Inorg. Chem.*, 1967, **6**, 258; (c) C.J. Jones and J.A. McCleverty, *J. Chem. Soc.*, (A). 1971, 1052; (d) N.A.H. Male, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487.

2 (a) J.L. Sessler and S.J. Weghorn, *Expanded, Contracted, and Isomeric Porphyrins*, Pergamon Press, Oxford, 1997; (b) A. Jasat and D. Dolphin, *Chem. Rev.*, 1997, **97**, 2267.

3 (a) N.A. Bailey, A. Barras, D.E. Fenton, M.S. Gonzales, R. Moody and C.O.R.D. Barbarin, *J. Chem.. Soc., Dalton. Trans.*, 1984, 2741; (b) S. Brooker and B.M. Carter, *Acat Cryst.*, 1995, **C51**, 1522; (c) M. Grigora, G. Stoica, I. Cianghe and C.I. Simionescu, *Rev. Roum. Chim.*, 1997, **42**, 993; (d) F. Franceschi, G. Guillemot, E. Solari, C. Floriani, N. Re, H. Birkedal and P. Pattison, *Chem. Eur. J.*, 2001, **7**, 1468; (e) M. Vazquez, M. Bermejo, M. Fondo, A. Garcia-Deibe, A.M. Gonzalez and R. Pedrido, *Eur. J. Inorg. Chem.*, 2002, 465; (f) A. Bacchi, M. Carcelli, L. Gabba, S. Ianelli, P. Pelagatti, G. Pelizzi and D. Rogolino. *Inorg. Chem. Acta.*, 2003, **342**, 229.

4 L. Yang, Q. Chen, G. Yang and J.S. Ma, *Tetrahedron*, 2003, **59**, 10037.

5 L. Yang, Q. Chen, Y. Li, S. Xiong, G. Li and J.S. Ma, *Eur. J. Inorg. Chem.*, 2004, 1478.

6 Z. Wu, Q. Chen, S. Xiong, B. Xin, Z. Zhao, L. Jiang and J.S. Ma, *Angew. Chem. Int. Ed.*, 2003, **42**, 3271.

7 L. Yang, X. Shan, Q. Chen, Z. Wang and J.S. Ma, *Eur. J. Inorg. Chem.*, 2004, 1474.

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

9 (a) G.R. Desiraju and T. Steiner, *The weak hydrogen bond in structural chemistry and biology*, Oxford University Press, Oxford, 1999; (b) D. Braga, F. Grepioni, E. Tegesco, K. Biradha and G.R. Desiraju, *Organometallics* 1997, **16**, 1846. (c) D. Braga, F. Grepioni and G.R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (d) L. Brammer, M.C. McCann, R.M. Bullock, R.K. McMullan and P. Sherwood, *Organometallics*, 1992, **11**, 2339; (e) E.O. Alyea, G. Ferguson and S. Kannan, *Chem. Commun.*, 1998, 345-346; (f) M. Brookhard and M.L.H. Green, *J. Organomet. Chem.*, 1983, 395.

10 (a) C.O. Dietrich-Buchecker, J.-P. Sauvage, J.-P. Kintzinger, P. Maltese, C. Pascard and J. Guilhem, *New J. Chem.* 1992, **16**, 931; (b) C.O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Armaroli, V. Balzani and L. De Cola, *J. Am. Chem. Soc.* 1993, **115,** 11237.