Directional self assembly of a double-helical complex of a solubilised septipyridine

Edwin C. Constable,* Markus Neuburger, Diane R. Smith and Margareta Zehnder

Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

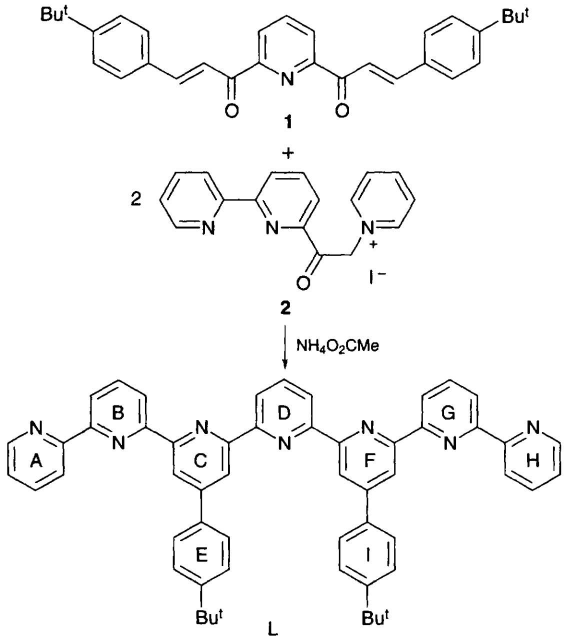
The solubilised septipyridine ligand L is prepared and reacts with zinc(II) acetate to give a head-to-head directional double helicate $[Zn_2L_2][PF_6]_4\cdot 6MeCN$ which is structurally characterised [space group $C2/c$, $a = 32.845(6)$, $b = 11.979(1)$, $c = 30.244(4)$ Å, $\beta = 95.79(1)°$, $R = 0.057$].

Oligopyridines and oligopyridine metal-binding domains have proved to be versatile and widely utilised motifs in metallosupramolecular chemistry.[1,2] We and others have probed the morphological variety which results from the interaction of the higher oligopyridines with metal ions.[1] An inherent problem with the higher oligopyridines is the great insolubility of the free ligands with associated difficulties of purification and characterisation. Various solubilisation strategies have been proposed[3,4] and we have now extended our approach[4] to the preparation of the 4-*tert*-butyl solubilised ligand L. In this paper we describe the synthesis of this compound and the unique self-assembly of the directional head-to-head dizinc double helicate $[Zn_2L_2]^{4+}$.

The new ligand L was prepared by the reaction of the bischalcone **1**[4] with 2 equiv. of the extended Krohnke reagent[5] **2** derived from 6-acetyl-2,2′-bipyridine[6] in the presence of ammonium acetate (Scheme 1). After recrystallisation from toluene, L was obtained as analytically pure colourless crystals in 56% yield.†

We have shown that oligopyridines form double-helicates upon coordination to zinc(II)[1,7] and anticipated the formation of $[Zn_2L_2]^{4+}$. However, only 12 of the total of 14 nitrogen donors will be involved in binding the two six-coordinate metal centres. Upon heating 1 equiv. of L with zinc acetate in methanol, a clear yellow solution was obtained from which a pale yellow solid $[(ZnL)_n][PF_6]_{2n}$ was precipitated upon the addition of NH_4PF_6. Mass spectrometric analysis indicated that the expected dinuclear species was present.‡

Recrystallisation yielded X-ray quality crystals of the complex $[Zn_2L_2][PF_6]_4\cdot 6MeCN$§ and the molecular structure of



Scheme 1

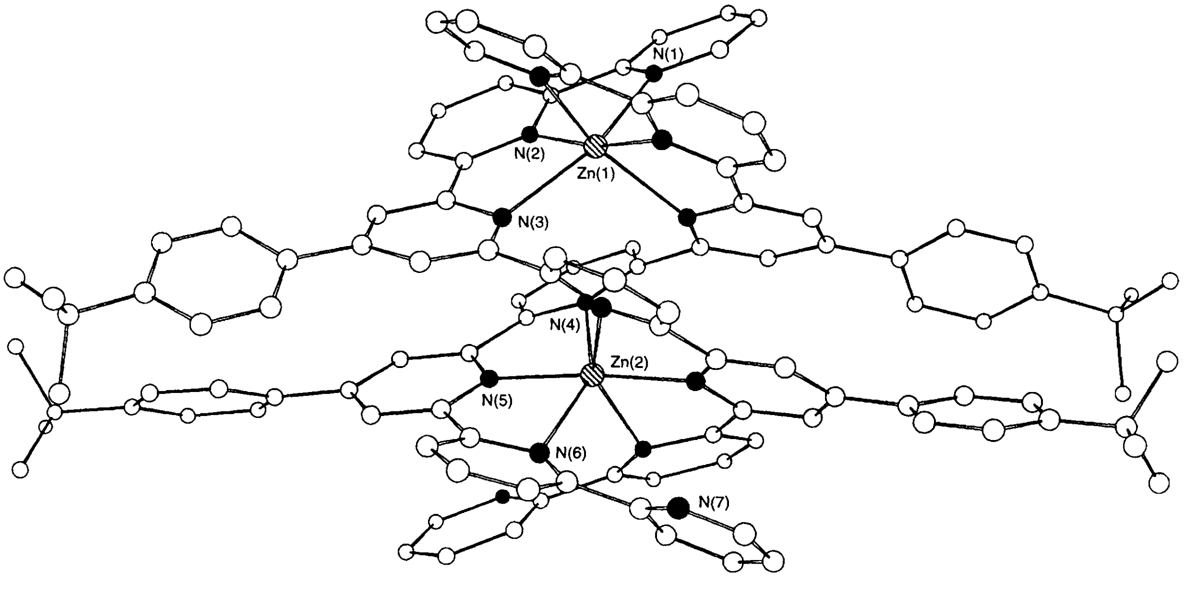


Fig. 1 Crystal and molecular structure of one enantiomer of the cation present in $[Zn_2L_2][PF_6]_4\cdot 6MeCN$. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Zn(1)–N(1) 2.222(3), Zn(1)–N(2) 2.070(3), Zn(1)–N(3) 2.259(3), Zn(2)–N(4) 2.262(3), Zn(2)–N(5) 2.015(3), Zn(2)–N(6), 2.394(3).

one of the enantiomers of the double-helical cation present in the lattice is shown in Fig. 1. Each zinc centre is six-coordinate with Zn–N distances in the expected range 2.015(3)–2.394(3) Å. The two ligand strands are equivalent and adopt a head-to-head arrangement with the terminal pyridine ring H of each uncoordinated. The helication arises as a result of twisting about the interannular bond between rings C and D of 47.4°; the angles between adjacent chelated rings are all $< 15°$ with the exception of that between F and G of 23.6°. The non-coordinated ring H makes a dihedral angle of 28.4° with ring G. The intermetallic distance is 4.333 Å. The formation of the single directional isomer is remarkable in view of the fact that the only other fully characterised complex of a septipyridine ligand contains two non-equivalent ligand strands, one with the non-coordinated ring in the middle and the other at an end. Modelling studies suggest that the selectivity arises from steric interactions between the bulky substituents, although we have recently shown that the origins of directional selectivity are complex.[6,10]

Although a single isomer is present in the solid state, the solution structure of the complex is less readily understood. The ^{1}H NMR spectra of crude precipitated product and recrystallised material were identical and showed a single solution species. The ^{1}H NMR spectrum of a CD_3CN solution of the complex shows the presence of 14 proton environments (assigned by COSY spectroscopy). These spectra are only consistent with the solution species being symmetrical with both ends of each ligand in an identical environment, *i.e.* the time-averaged solution and solid-state species are different. We note that H^{5A} appears upfield of H^{6A} which is the reverse of the situation observed in other dizinc helicates[1,7] and more reminiscent of a free ligand. Resonances associated with the internal rings of each strand show no abnormal shifts. This suggests a degree of 'free' non-coordinated character associated with the terminal rings and we propose a solution equilibrium between head-to-head and tail-to-tail isomers. Variable-temperature ^{1}H NMR experiments (293–245 K) showed the complex to be fluxional with a gradual disappearance and downfield shift of the protons associated with terminal pyridine observed on cooling the sample, but we were unable to reach a coalescence or frozen-out species. We are currently further investigating the solution properties of this and related complexes.

We should like to thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant numbers: 21-37325.93, 20-43359.95) and the European community (associated contract CEC ERBCHRXCT 940492/A2) for support.

Footnotes

† A suspension of **1** (0.11 g, 0.25 mmol), **2** (0.20 g, 0.50 mmol) and anhydrous ammonium acetate (0.19 g, excess) in ethanol (20 cm^3) was heated at reflux for 14 h. On cooling, the white precipitate was filtered off and recrystallised from toluene to yield **1** (0.11 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (s, 18 H, Bu^t), 7.37 (m, 4 H, H^{5A}, $H^{3B/5B}$) 7.61 (d, 4 H, H^{3E}), 7.96 (m, 6 H, H^{2E}, H^{4A}), 8.06 (t, 1 H, H^{4D}), 8.12 (t, 2 H, H^{4B}), 8.53 (m, 2 H, H^{6A}), 8.73 (m, 4 H, H^{3A}, $H^{3B/5B}$), 8.95 (d, 2 H, $H^{3C/5C}$), 9.05 (d, 2 H, $H^{5C/3C}$). EIMS: *m/z* 806 (M^+).

‡ L (0.030 g, 0.04 mmol) and $Zn(O_2CMe)_2 \cdot 4H_2O$ (0.01 g, 0.04 mmol) in MeOH (5 cm^3) were heated at reflux for 1 h. After cooling, a methanolic solution of NH_4PF_6 was added and the resulting precipitate isolated by filtration and recrystallised by the diffusion of diethyl ether vapour into an acetonitrile solution to give pale yellow crystals of $[Zn_2L_2][PF_6]_4 \cdot 6MeCN$ (0.030 g, 70%). ^{1}H NMR (250 MHz, CD_3CN): δ 1.47 (s, 18 H, Bu^t), 6.96 (m, 2 H, H^{5A}), 7.20 (m, 2 H, H^{6A}), 7.49 (td, *J* 6, 1.6 Hz, 2 H, H^{4A}), 7.59 (d, *J* 8 Hz, 2 H, H^{3D}), 7.66 (m, 6 H, H^{3E}, H^{3A}), 7.77 (m, 4 H, H^{2E}), 7.85 (t, *J* 8 Hz, 1 H, H^{4D}), 8.10 (m, 8 H, H^{3B}, H^{5B}, H^{3C}, H^{SC}), 8.18 (t, *J* 8 Hz, 2 H, H^{4B}), H^{3B} and H^{5B} unassigned. TOFMS: *m/z* 2173 $\{[Zn_2L_2][PF_6]_3\}$, 1965 $\{[ZnL_2][PF_6]\}$.

§ *Crystal data*: pale yellow crystal, $C_{122}H_{112}F_{24}N_{20}P_4Zn_2$, $M = 2568.98$, monoclinic, space group *C2/c*, $a = 32.845(6)$, $b = 11.979(1)$, $c = 30.244(4)$ Å, $\beta = 95.79(1)°$, $U = 11838(3)$ Å^3, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $F(000) = 5280$, $\lambda = 1.54180$ Å, μ(Cu-Kα) 1.84 mm^{-1}. Intensity data were collected by the ω-scan method ($0 < 2\theta < 155°$); for a crystal of dimensions 0.21 × 0.30 × 0.40 maintained at 223 K; of 10111 (9715 independent) reflections measured, 6640 were used in the structure solution (Chebychev polynomial weighting: J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698). The structure was solved (direct methods) and refined using CRYSTALS to give final *R* and R_W values of 0.0571 and 0.0505 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/167.

References

1 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013; *Prog. Inorg. Chem.*, 1994, **42**, 67.

2 F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1993; J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.

3 K. T. Potts, K. A. G. Raiford and M. Keshavarz-K, *J. Am. Chem. Soc.*, 1993, **115**, 2793.

4 E. C. Constable, P. Harverson, D. R. Smith and L. A. Whall, *Tetrahedron*, 1994, **50**, 7799.

5 F. Krohnke, *Synthesis*, 1976, 1.

6 E. C. Constable, F. Heirtzler, M. Neuburger and M. Zehnder, *J. Am. Chem. Soc.*, submitted for publication; J. E. Parks, B. E. Wagner and R. H. Holm, *J. Organomet. Chem.*, 1973, **56**, 53.

7 E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1996, 2423.

8 R. Chotalia, E. C. Constable, M. Neuburger, D. R. Smith and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, in the press.

9 K. T. Potts, M. Keshavarz-K, F. S. Tham, K. A. G. Raiford, C. Arana and H. D. Abruna, *Inorg. Chem.*, 1993, **32**, 5477.

10 E. C. Constable, F. R. Heirtzler, M. Neuburger and M. Zehnder, *Supramol. Chem.*, 1995, **5**, 197; *Chem. Commun.*, 1996, 933.

Received, 4th June 1996; Com. 6/03899I