This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Directional ligands in helicate selfassembly

Edwin C. Constable[a]; Fenton R. Heirtzler[a]; Markus Neuburger[a]; Margaret Zehnder[a]
[a] Institut für Anorganische Chemie der Universität Basel, Basel, Switzerland

To cite this Article Constable, Edwin C. , Heirtzler, Fenton R. , Neuburger, Markus and Zehnder, Margaret(1995) 'Directional ligands in helicate selfassembly', Supramolecular Chemistry, 5: 3, 197 — 200

To link to this Article: DOI: 10.1080/10610279508028947

URL: http://dx.doi.org/10.1080/10610279508028947

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 197–200
Reprints available directly from the publisher
Photocopying permitted by license only

COMMUNICATION

Directional ligands in helicate self-assembly

EDWIN C. CONSTABLE*, FENTON R. HEIRTZLER, MARKUS NEUBURGER and MARGARET ZEHNDER

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

(Received November 7, 1994)

The new asymmetric ligand 4-methyl-4'-ethylthio-2,2':6',2":6",2'"-quaterpyridine (L) has been prepared and structurally characterised (triclinic, $P\bar{1}$, $a = 9.114(1)$, $b = 10.790(1)$, $c = 10.954(1)$ Å, $\alpha = 78.565(6)$, $\beta = 71.759(7)$, $\gamma = 89.497(5)$ °, $V = 1001.18(2)$ Å^3, $Z = 2$, $R_W = 0.087$); the helicates $[Cu_2L_2]^{2+}$ are formed with a 2:3 preference for the less hindered isomer).

The assembly of helicates from the interaction of multiple domain ligands with metal ions is well established.[1] Oligopyridines and ligands containing multiple oligopyridine domains have proved to be valuable helicands, and have allowed us to develop an understanding of the processes controlling helicate assembly. Although systematic approaches have been developed for the synthesis of heterodinuclear double helicates,[2] little attention has been given to double helicates with asymmetric ligand strands.[3] In this paper we describe the synthesis of a first generation directional ligand strand, and report upon its helication behavior.

2,2':6',2":6",2'"-Quaterpyridine (qtpy) acts as a prototype helicand, which can present two didentate (bpy-like) domains to two *pseudo*tetrahedral metal centres to form a double helicate.[4] If substituents are introduced asymmetrically, the ligand strand has a sense of directionality. Upon formation of a double helicate with copper(I) or silver(I), such a ligand could give head-to-head (**HH**) or head-to-tail (**HT**) helicates (Fig. 1) depending upon whether the substituted rings in each ligand strand are coordinated to the *same* or to *different* metal centres. Modelling studies indicate that selectivity between the formation of these two helicates might be realised by the introduction of sterically demanding substituents upon the 4-position of the terminal pyridine rings. Substitution at this position should lead to minimal *intramolecular* interactions within each ligand strand but maximal *intermolecular* interactions in the **HH** double helicate (Fig 2a) should be observed. In contrast, the intramolecular interactions should be smaller in the **HT** isomer (Fig. 2b). Such a situation is expected to lead to a preference for the **HT** isomer over the **HH**.

Our first generation directional strand was 4-methyl-4'-ethylthio-2,2':6',2":6",2'"-quaterpyridine (L),[5] which was prepared in 31% yield from 6-acetyl-2,2'-bipyridine and the diethylthioketene acetal of 2-acetyl-4-methylpyridine using Potts' methodology[6] (Scheme 1). In order to verify that no significant structural perturbation of the ligand had occurred, we have determined the crystal structure of the new ligand, L (Fig. 3).[7] In the solid state, there are no close contacts between the substituents, and the ligand adopts the expected[10] *trans, trans, trans* conformation about the interannular C-C bonds. All bond lengths and angles are within the usual expected limits and closely resemble those found in qtpy.[10] There are graphitic interactions between planar molecules in adjacent lattice planes, and also a short contact (3.77 Å) between the sulfur atom of one ligand and ring C of the stacked ligand in the adjacent plane.

The reaction of L with $[Cu(MeCN)_4][PF_6]$ in hot MeOH gave a brown solution from which the complex $[Cu_2L_2][PF_6]_2$ could be isolated as a brown solid. Microanalysis indicated that no solvent was present in the lattice. The FAB mass spectrum of the complex ex-

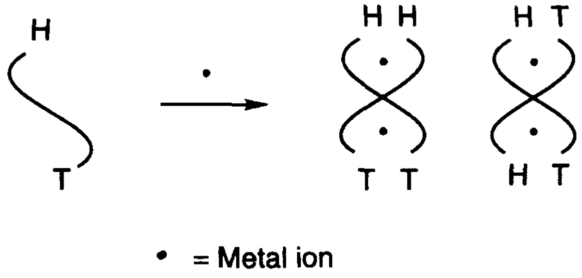


Figure 1 The assembly of isomeric head-to-head (**HH**) and head-to-tail (**HT**) helicates from directional helicands.

---

* To whom correspondence should be addressed.

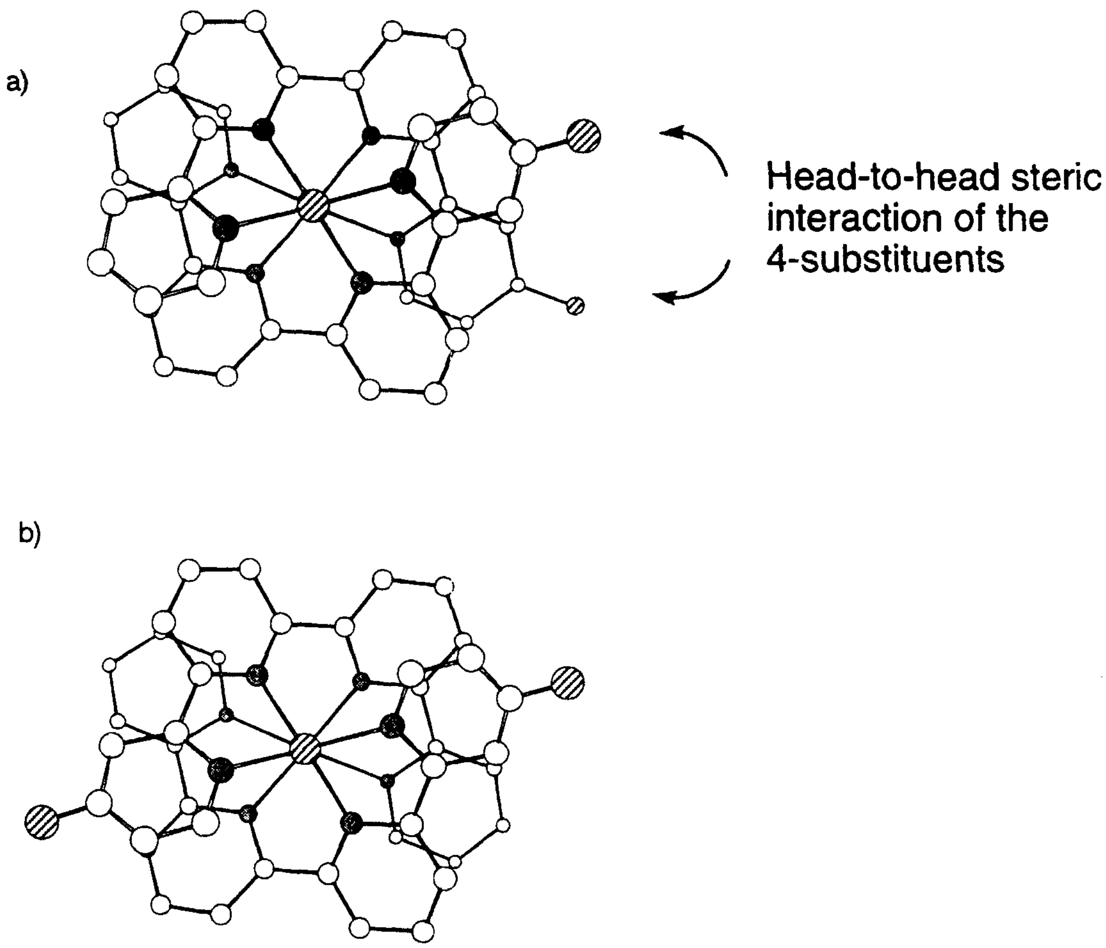
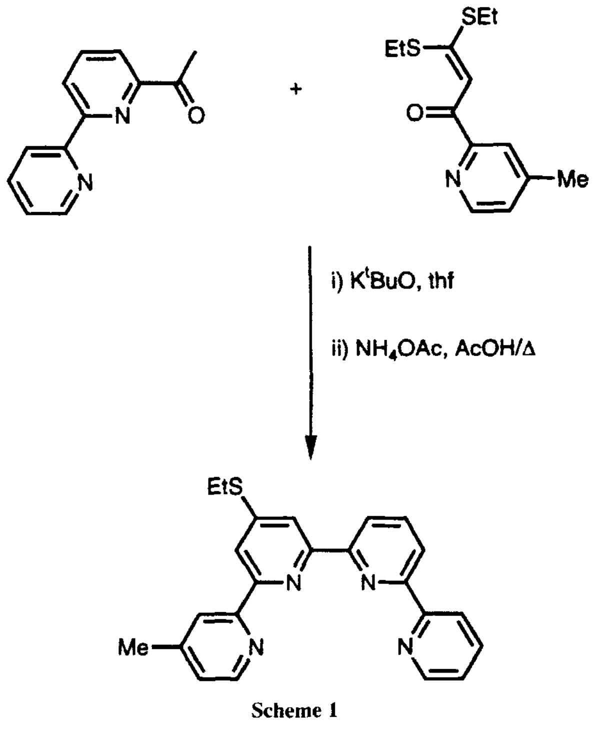


Figure 2 A view along the metal-metal axis of an $M_2(qtpy)_2$-type helicate showing the steric interactions between groups in the 4-position in a) the **HH** and b) the **HT** isomers.



Scheme 1

hibits prominent clusters of ions at *m/z* 1041 ($\{Cu_2L_2(PF_6)\}^+$) and *m/z* 447 ($\{CuL\}^+$). The coordination of all four nitrogen donors of a qtpy ligand to a single tetrahedral copper(I) centre is geometrically impossible and all known complexes of the type $\{Cu(qtpy)\}_nX_n$ containing non-coordinating anions are double-helical $[Cu_2(qtpy)_2]^{2+}$ species.[4,11] The compound elutes as a single spot on TLC (Rf = 0.53: silica gel, 7:1:0.5 CH_3CN:saturated aqueous KNO_3: H_2O). We are thus confident that our new $[Cu_2L_2][PF_6]_2$ complex is double helical and can exclude the formation of a mixture of dinuclear and other mononuclear species. The ^1H NMR spectrum of a solution of $[Cu_2L_2][PF_6]_2$ in CD_3CN is complex, and there are many overlapping resonances in the aromatic region. In general, all protons are represented by resonance pairs, assigned to the **HH** and **HT** isomers. However, *two* well-resolved resonances are observed at $\delta = 2.45$ and 2.50 in a ratio 2:3[12] and are assigned to the 4-methyl group of the pyridine ring (Fig. 4). Two unequal resonances are also observed for the methyl group in the ^{13}C NMR spectrum of the complex. This is consistent with the formation of both the **HH** and **HT** isomers of the double helix. In each case, the methyl

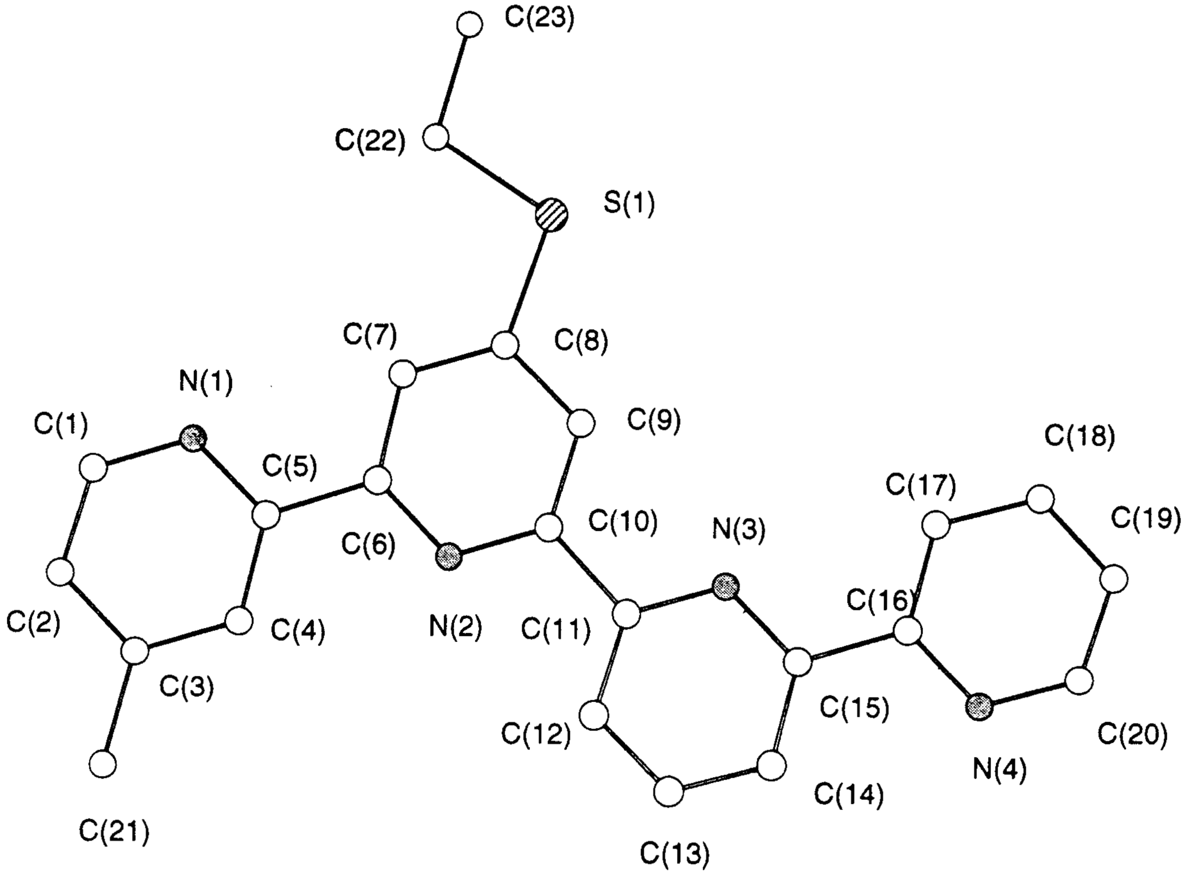


Figure 3 The crystal and molecular structure of L showing the labelling scheme adopted. Hydrogen atoms have been omitted for clarity.

groups of the two strands in the complex are chemically and magnetically equivalent. For the reasons discussed above, we can eliminate possibilities of a mixture of mono- and dinuclear solution species. We interpret the data in terms of a selective formation of the **HT** isomer which does not exhibit the interstrand methyl-methyl interactions which are found in the **HH** isomer. We should stress that the NMR experiments do not unambiguously establish which is the predominant isomer, but in the absence of solid state structural data we presume it to be the sterically favoured **HT** form.

In conclusion, our first generation asymmetrical ligand demonstrates a selectivity for the formation of the **HT** double helix. We are presently unable to state whether the two isomers are in dynamic equilibrium. We are currently addressing this question and preparing new ligands containing bulkier substituents or strongly electron-donating and -withdrawing substituents to maximise pairwise charge-transfer interactions.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant number: 21-37325.93) and the University of Basel for financial support.

REFERENCES

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

2 Constable, E.C.; Walker, J.V. *J. Chem. Soc., Chem. Commun.* **1992**, 884; Constable, E.C.; Edwards, A.J.; Raithby, P.R.; Walker, J.V. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1465.

3 Piguet, C; Bocquet, B.; Hopfgartner, G. *Helv. Chim. Acta* **1994**, *77*, 931.

4 Constable, E.C.; Hannon, M.J.; Tocher, D.A. *Polyhedron* **1992**, *11*, 2967.

5 mp = 164–165° C; ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 8.67 (br d, $H_{6'''}$), 8.63 (br d, J ~7 Hz, $H_{3''/5''}$), 8.61 (d, J ~7 Hz, $H_{3'''}$), 8.53 (d, J = 5.2 Hz, H_6), 8.49 (d, J = 1.8 Hz, $H_{3'/5'}$), 8.47 (d, J ~8 Hz, $H_{5''/3''}$), 8.43 (s, H_3), 8.33 (d, J = 1.8 Hz, $H_{5'/3'}$), 7.89–8.03 (m, $H_{4''}$), 7.84–7.89 (m, $H_{4'''}$), 7.34 (dd, J = 7.5 Hz, $H_{5'''}$), 7.15 (br d, J ~4 Hz, H_5); 3.22 (q, J = 7.3 Hz, SCH_2), 2.48 (s, CH_3), 1.48 (t, J = 7.3 Hz, CH_2CH_3): EI-MS (70 eV): *m/z* (%) = 384 (M^+, 76), 369 (17), 356 (100), 351 (32), 324 (31), 312 (15), 205 (12), 192 (11), 178 (13), 155 (9).

6 Potts, K.T.; Cipullo, M.J.; Ralli, P.; Theodoridis, G. *J. Org. Chem.* **1982**, *47*, 3027; *J. Am. Chem. Soc.* **1981**, *103*, 3585; Potts, K.T.; Gheysen Raiford, K.A.; Keshavarz-K, M. *J. Am. Chem. Soc.* **1993**, *115*, 2793.

7 *Crystal data* for $C_{23}H_{20}N_4S$, M = 384.498, triclinic, $P\bar{1}$, a = 9.114(1), b = 10.790(1), c = 10.954(1) Å, α = 78.565(6), β = 71.759(7), γ = 89.497(5) °, V = 1001.18(2) Å^3, D_c = 1.275 g cm^{-3},

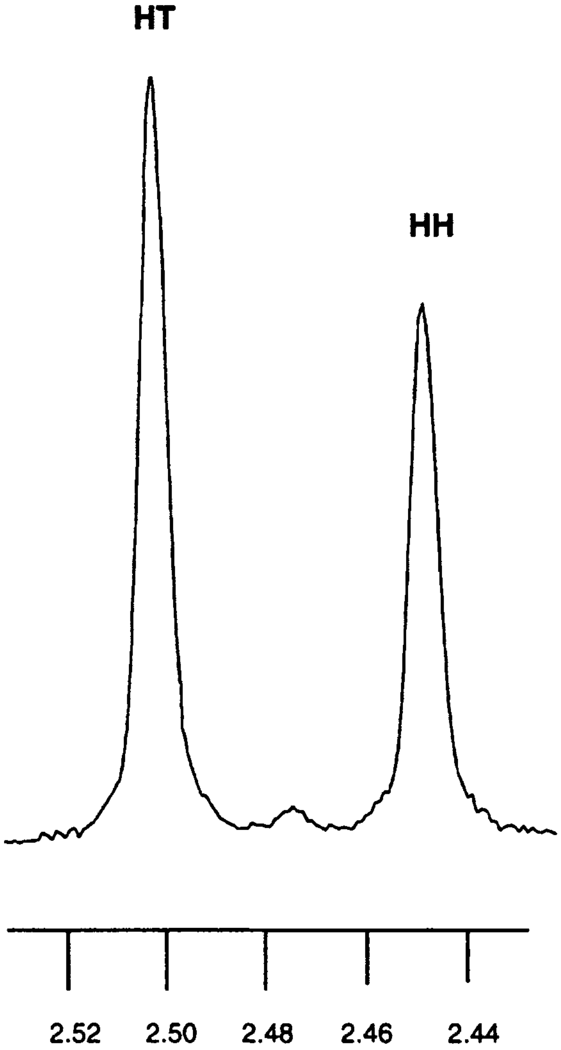


Figure 4 The methyl region of the 300 MHz ^{1}H NMR spectrum of a CD$_3$CN solution of [Cu$_2$L$_2$][PF$_6$]$_2$ showing the two isomers.

$Z = 2$, $\mu = 15.061$ cm^{-1}, crystal dimensions $0.08 \times 0.24 \times 0.28$ mm. θ max = 74.33°, λ (Cu-K$_\alpha$) = 1.54178Å, $\omega/2\theta$ scan technique, 4090 independent reflections, 2552 reflections used in refinement, final $R_w = 0.087$, weighting scheme $[1-(\Delta(F)/6\sigma(F)^2]^2$. Diffraction absorption correction was determined by ϕ scans. The hydrogen atoms are included in calculated positions. The structure was solved by direct methods using SHELXS-86[8] and refined using CRYSTALS.[9]

8 SHELXS-86, Sheldrick, G.M. University of Göttingen, **1986.**

9 CRYSTALS, Issue 9, Watkin, D.; Chemical Crystallography Laboratory, Oxford, 1990.

10 Constable, E.C.; Elder, S.M.; Healy, J.A.; Tocher, D.A. *J. Chem. Soc., Dalton Trans.* **1990**, 1669.

11 Lehn, J.-M.; Sauvage, J.-P.; Simon, J.; Ziessel, R.; Piccinni-Leopardi, C.; Germain, G.; Declercq, J-P.; Van Meerssche, M. *Nouv. J. Chim.* **1983**, *7*, 413; Gisselbrecht, J.-P.; Gross, M.; Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R.; Piccinni-Leopardi, C.; Arrieta, J.M.; Germain, G.; Van Meerssche, M. *Nouv. J. Chim.* **1984**, *8*, 661; Arnaud-Neu, F.; Sanchez, M.; Schwing-Weill, M.-J. *New J. Chem.* **1986**, *10*, 165; Potts, K.T.; Keshavarz-K, M.; Tham, F.S.; Abruña, H.D.; Arana, C.R. *Inorg. Chem.* **1993**, *32*, 4422.

12 The two methyl resonances are observed in a ratio of 2:3 by integration: this ratio remained constant in a spectrum accumulated with long delays between adjacent pulses to eliminate relaxation effects.