Writing and Revising
the Disciplines

Edited by

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Writing (and Drawing) Chemistry

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In the chemical profession our stock in trade is not the book, but the scientific (chemical) article, published in a periodical. I have written 450 of them in my years at Cornell University; my colleague Harold Scheraga has published over 1000. We have promoted an assistant professor to tenure at Cornell with 11 published papers, and we have not promoted one with over 80.

THE NATURE OF THE BEAST

It is instructive to see the article untamed, roaming its range. For this I would like to begin with some pages from the chemical journal that is arguably the world's best (at least in inorganic and organic chemistry, not in physical chemistry or biochemistry); publication venues and their prestige carry much baggage of history and fashion. The journal is not an American one. It is *Angewandte Chemie*, published out of Germany, it appears simultaneously in German and English editions. Despite its name, the journal contains precious little applied chemistry.

Angewandte Chemie, under the inspired and proactive leadership of its editor, Peter Gölitz, has cultivated an effective mix of largely solicited review or feature articles, short highlights, and many "Communications." These are brief accounts of novel chemistry, presumably worthy of urgent publication. And publication, following review by one to three anonymous (to the author) referees, is certainly rapid. Several Communications in the Nov. 2, 1998 issue of the journal carry June submission dates; the latest is dated July 1, 1998. For my friends in the humanities (I'm there

too; I have been waiting over two years for a paper to appear in the *Canadian Review of Comparative Literature*), all I can say is "It can be done."

Let us leaf (see figures 1–5) through some pages in the Nov. 2, 1998 issue of *Angewandte Chemie* which arrived in my mailbox the week of November 9. (The original lecture on which this text is based was presented on Nov. 16, 1998.)

From these five sequential pages, as well as perusal of a greater sample, one notes:

(1) The authorship is international.

(2) There are many authors per paper; one of the differences between the sciences and the humanities and arts (theater and film are exceptions), is that the sciences have mastered the ethics of collaboration.

(3) The usual scholarly apparatus is there: author affiliations, endnotes (often numerous), acknowledgments of granting agencies and individual assistance or discussion.

(4) An unusual feature, particular to *Angewandte Chemie*, is the mandatory inclusion at the end of any experimental paper of an experimental section, detailing procedures for at least part of the experiments carried out.

(5) Most striking is the remarkable density of graphic material, most of it quasi-iconic representations of microscopic molecular structure. It is this feature of chemistry—the high graphical content of the literature and the science—which led me to include the parenthetical clause in my title (see Hoffmann and Laszlo, 1991). I will return to it, for now I hope I have convinced you that it is not my stylistic prejudice when I say that it is impossible to write chemistry without drawing molecules.

I also note that while there are some graphs and plots of observables, these are relatively few. And still fewer equations. This is not physics.

Is what these figures present typical? Yes, it certainly is so, of the literature of organic, inorganic, and biological chemistry. Physical chemistry is quite different, for its literature (viewed phenomenologically) carries more equations, and fewer depictions of molecules.

CALIXARENES

Let us now zoom in on one article, and read it together. I do this for the ostensible reason of analyzing this contemporary text as a text. But I must also 'fess up; I do it because I will not pass up the chance of teaching any audience, including the audience of the present volume, some chemistry.

COMMUNICATIONS

A New Motif for the Self-Assembly of [2]Pseudorotaxanes; 1,2-Bis(pyridinium)ethane Axles and [24]Crown-8 Ether Wheels**

Stephen J. Loeb* and James A. Wisner

The threading of the paraquat dication PQT^{2+} through the cavity of bis(paraphenylene)[34]crown-10 (BPP34C10) to form the [2]pseudorotaxane [(BPP34C10)(PQT)]$^{2+}$ (**1**) was the genesis of a diverse range of molecules that contain mechanical linkages (rotaxanes, catenanes, molecular shuttles, and switches) derived from this basic interaction, and stands as a landmark discovery in the area of supramolecular chemistry (Scheme 1).[1] Many examples of rotaxanes have


BPP34C10

+

PQT^{2+}

↓

1
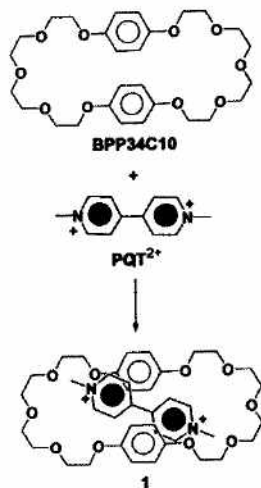
Scheme 1. Formation of the [2]pseudorotaxane **1** by insertion of the linear dicationic axle PQT^{2+} through the cavity of the neutral crown ether wheel BPP34C10.
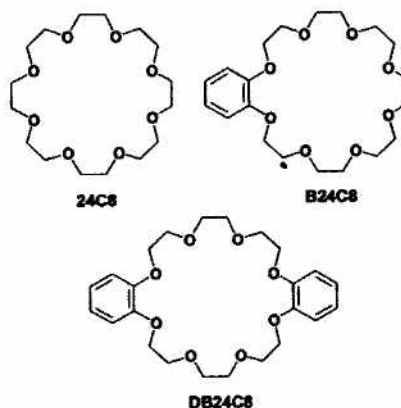
now been reported involving π stacking between electron-rich and electron-poor aromatic rings,[2] hydrogen bonding between secondary dialkylammonium ions and crown ethers[3] or between amides and large ring lactams,[4] hydrophobic interactions within the cavity of a cyclodextrin,[5, 6] and metal–ligand interactions between transition metal ions and cyclic ligands.[7-9] In many of these systems the ion–dipole interaction between positively charged atoms of one component and the Lewis basic atoms of the other component makes a significant contribution to the binding. Although these electrostatic interactions are not directional and predictable in the same manner as hydrogen bonds or metal–ligand

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bonds, they are nonetheless extremely important. For example, the PQT^{2+} ion in **1** is tilted away from perpendicular by 62° so as to maximize the N$^+$···O interactions and also form weak CH···O hydrogen bonds along with the major π-stacking components.[1]

Herein, we present a new motif for the design of [2]pseudorotaxanes based on the simple concept of optimizing N$^+$···O interactions between pyridinium ions and simple crown ethers.[10] The N$^+$–N$^+$ distance in PQT^{2+} is about 7.00 Å while in the isomeric 1,2-bis(pyridinium)ethane dication **2a** it is only about 3.75 Å (Scheme 2). Although Stoddart et al. have reported that the interaction between dibenzylparaquat and DB24C8 is negligible,[11, 12] an examination of CPK and computer models suggested a good match between **2a** (the "axle") and the 24-membered crown ethers (wheels) 24C8, B24C8, and DB24C8 (Scheme 3) that should

PQT^{2+}

|← 7.00 Å →|

|← 3.75 Å →|

2a
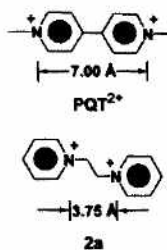
Scheme 2. Comparison of the intramolecular N$^+$–N$^+$ distances in the isomeric pyridinium ions PQT^{2+} and [pyCH$_2$CH$_2$py]$^{2+}$ (**2a**).

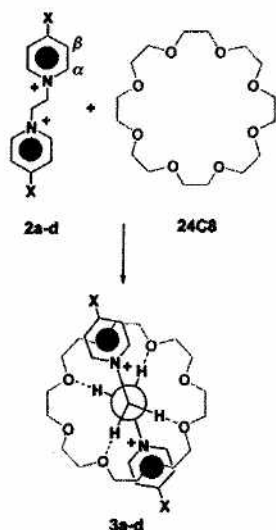optimize the N$^+$···O interactions. Scheme 4 shows how two sets of N$^+$···O interactions might be accompanied by a series of four C–H···O hydrogen bonds that are formed with alternate oxygen atoms in the crown ether. The question remains as to whether these interactions are sufficient to produce a stable [2]pseudorotaxane in the absence of the π-stacking interactions found in **1** and related molecules.

The addition of one equivalent of 24C8 to a solution of one equivalent of **2a**(BF$_4$)$_2$ in MeCN gave the [2]pseudorotaxane **5a**. An association constant K_a of 165 M^{-1} was measured for this interaction by ^{1}H NMR titration in MeCN at 298 K. By variation of the substituent X on the pyridinium ring other axles can be incorporated and a more detailed understanding of the overall interaction can be obtained. The strength of the interaction can be controlled by varying X as shown in Table 1. In particular, the introduction of the electron-with-

24C8   **B24C8**

DB24C8

Scheme 3. Formation of [2]pseudorotaxanes from 24C8, B24C8, and DB24C8.

FIGURE 1

Scheme 4. Newman projection along the C–C vector of the N⁺CH₂CH₂N⁺ portion of the dication [XpyCH₂-CH₂pyX]²⁺, 2a–d, (X = H, Me, Ph, CO₂Et,). This combination of N⁺···O ion–dipole interactions and C–H···O hydrogen bonds might stabilize the formation of [2]pseudorotaxanes with 24C8.

drawing group CO_2Et results in the largest association constant for the interactions with each of the three crown ethers.

Incorporation of aromatic groups into the crown ether provides the possibility of π stacking between the pyridinium rings and the catechol rings of the crown ether. In the ¹H NMR spectra of the two pseudorotaxanes derived from 2a (X = CO_2Et) with B24C8 (4d) and DB24C8 (5d) π stacking in solution is clearly evident: the signals for the β protons of the pyridine group shift upfield ($\delta = 8.56$, 8.36, and 8.14 for the pseudorotaxanes with 24C8, B24C8, and DB24C8, respectively). This trend is mirrored by a uniform increase in K_a from 320 to 740 to $1200\,\text{M}^{-1}$ and an increase in the intensity of a charge transfer absorption band at about 370 nm (Figure 1). In addition, 3d–5d show significant downfield shifts ($\delta = $

0.20–0.31)for the α and NCH_2 protons, which is indicative of the formation of C–H···O hydrogen bonds to the oxygen atoms of the crown ether.

These results and the threading conformation proposed in Scheme 4 are supported by the solid-state structure of [(EtO₂CpyCH₂-CH₂pyCO₂Et)(DB24C8)]²⁺ (5d; py = C₅H₄N⁺).[13] Figures 2 and 3 show different views of the threading of the dicationic axle through the cavity of the DB24C8 macrocycle. The [2]pseudorotaxane is stabilized by 1) eight N⁺···O interactions (N–O 3.76–4.88 Å), 2) eight C–H···O hydrogen bonds (the four predicted ones between the bridging ethane unit and alternate ether oxygen atoms as well as four others between α-pyridinium hydrogen atoms and symmetry related O5 atoms
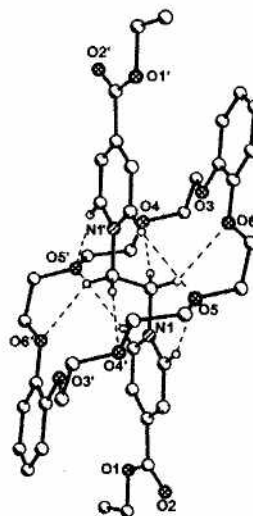
Figure 2. A ball-and-stick representation of the crystal structure of 5d, formed from [EtO₂CpyCH₂-CH₂pyCO₂Et]²⁺ (2d) and DB24C8.

Figure 3. A ball-and-stick representation of the crystal structure of 5d, shown along the C9–C9' bond. This view corresponds to the Newman projection show schematically in Scheme 4. N⁺–O distances: N1⁺–O3 4.88, N1⁺–O4 4.43, N1⁺–O5 3.76, N1⁺–O6 4.66 Å. C–H···O hydrogen bonds (lengths [Å] and angles [°]): H9A–O4' 2.54, H9B–O6' 2.66, H6A–O5 2.36, H7A–O5' 2.54; C9-H9A-O4' 165.0, C7-H7A-O5' 141.0, C6-H6A-O5 154.2, C9-H9B-O6' 150.0.
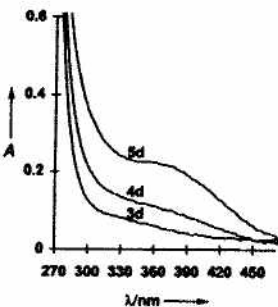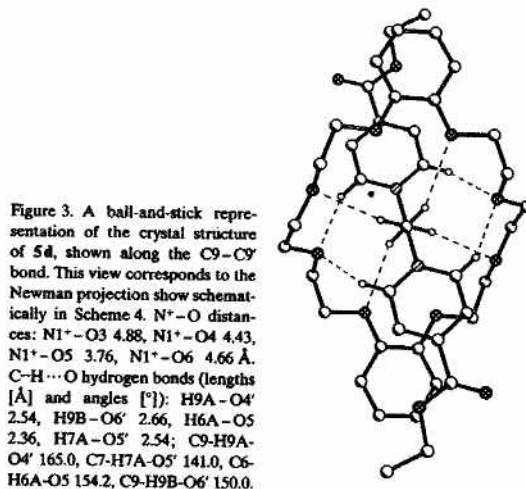

Figure 1. UV absorption spectra of 3d, 4d, and 5d. The intensity of the charge-transfer band in the region 270–470 nm increases with increased capacity for π-stacking interactions.

Table 1. Association constants (K_a) and free energies of complexation (ΔG) for 3a–d, 4a–d, and 5a–d formed from [X-pyCH₂CH₂py-X]²⁺, 2a–d, and 24C8, B24C8, or DB24C8 in MeCN at 298 K.[a]

X	24C8		B24C8		DB24C8	
	K_a [M⁻¹]	$-\Delta G$ [kJ mol⁻¹]	K_a [M⁻¹]	$-\Delta G$ [kJ mol⁻¹]	K_a [M⁻¹]	$-\Delta G$ [kJ mol⁻¹]
H (a)	165	12.7	195	13.1	180	12.9
Me (b)	105	11.6	205	13.2	230	13.5
Ph[b] (c)	160	12.6	300	14.2	320	14.3
CO₂Et[b] (d)	320	14.3	740	16.4	1200	17.6

[a] Sample concentrations $2.0 \times 10^{-3} - 5.0 \times 10^{-3}$ M. [b] Chemical exchange was slow on the NMR time scale and peaks were observed for both complexed and uncomplexed species. K_a was determined by integration from a 1:1 mixture. All other K_a values were determined by NMR titration experiments by using the program EQNMR.[16] Estimated errors: <10% for $K_a > 100$.

FIGURE 2

(C–O 2.36–2.66 Å), and 3) π-stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poor aromatic rings and ester group of the pyridinium salt.

The new binding motif for the formation of [2]pseudorotaxanes presented herein demonstrates for the first time that simple crown ethers can be used to form [2]pseudorotaxanes. The ability to easily tune the interaction strength and the availability of these simple components bodes well for the extension of this motif to more complex supramolecular systems with interlocked [n]rotaxanes and [n]catenanes.

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[10] For a recent example of host–guest interactions between crown ethers and pyridinium compounds, see M. Lämsä, J. Huuskonen, K. Rissanen, J. Pursiainen, *Chem. Eur. J.* **1998**, *4*, 84–92.

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J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 1387–1388.

[13] Crystal structure data for **5d**(BF$_4$)$_2$: monoclinic, space group $P2_1/c$, a = 13.2421(4), b = 15.7037(5), c = 12.1739(4) Å, $β$ = 94.909(1)°, V = 2522.3(1) Å^3, Z = 2, $ρ_{calcd}$ = 1.308 g cm^{-3}, $2θ_{max}$ = 45.0°, Mo$_{Kα}$ radiation ($λ$ = 0.71073 Å), T = 296 K. A pale yellow crystal with dimensions 0.2 × 0.2 × 0.3 mm was grown by vapor diffusion of isopropyl ether into a solution of **5d** in MeCN and mounted on a fibre. The 3280 unique reflections (R_{int} = 0.0715) were integrated from frame data obtained from programmed hemisphere scan routine on a Siemens SMART CCD diffractometer. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Systematic absences in the diffraction data and determined unit-cell parameters were consistent with the space group $P2_1/c$. Lorentzian-polarization correction and semi-empirical absorption correction, based on redundant data at varying effective azimuthal angles, were applied to the data ($μ$ = 0.112 cm^{-1}, min./max. transmission = 0.221/0.492). The structure was solved by direct methods, with Fourier syntheses, and refined with full-matrix least-squares methods against $|F^2|$ data to give $R(F)$ = 0.0815, $wR(F^2)$ = 0.2271, GOF = 1.033, N_o/N_v = 3275/354. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101459. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[Te$_6$N$_8$(TeCl$_4$)$_4$]—Tellurium Nitride Stabilized by Tellurium Tetrachloride

Werner Massa, Carsten Lau, Michael Möhlen, Bernhard Neumüller, and Kurt Dehnicke*

Exactly 100 years ago tellurium nitride was first obtained by the reaction of tellurium tetrabromide with liquid ammonia.[1] The composition TeN was ascribed to this yellow, extremely poorly soluble, and highly explosive substance. Considering the analogy to the crystallographically well characterized homologues S$_4$N$_4$[2] and Se$_4$N$_4$,[3] this assignment has not been entirely ruled out to this day.[4] However, later analytical work made the composition Te$_3$N$_4$ with tetravalent tellurium probable.[5-7] The tellurium compounds with nitride functionalities which were characterized in recent years also derive from tellurium(+IV). Among these are the complexes of type 1 with X = Cl[8] and F,[9] which correspond to the structure motif A with pyramidal nitride functionality, and the nitride

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FIGURE 3