Please read the attached JACS communication and answer the following questions about the paper. You have 2 hours for this closed book exam.

1. (10 pts) In the first sentence the authors refer to “ion templation” as one of the driving forces controlling the self-assembly process. Explain what “ion templation” is and give an example of how it affects self-assembly.

2. (10 pts) Prof. Dunbar uses [Ni(MeCN)₆][SbF₆]₂ as the starting material for her synthesis of the molecular pentagons. Sketch the structure of this out (only the cation) and clearly show the electron-counting for the complex.
3. (20 pts) Explain and discuss the unusual electron-count on [Ni(MeCN)₆]²⁺. What does this imply about the bonding of the MeCN ligands? Is this important for the self-assembly of the molecular pentagons? Why? Neutral Ni(II) complexes with strong field ligands rarely contain more than five two-electron donor ligands. But dicationic Ni(II) complexes are more likely have six ligands around them in crystal structure determinations. Keep this in mind for your discussion.

4. (10 pts) What is the electron-count for the nickel centers in [I]¹⁰⁺? Sketch out the ligand environment around one nickel center showing the geometry and show the electron-count.
5. **(20 pts)** If one had a solution of compound 1 and you added excess NaClO₄, what complex would you expect to crystallize out of solution after several days of reaction? Discuss. How does this relate to your answer for question # 4.

6. **(20 pts)** On the second page the authors state: “Above 50K, χT is constant at ~5.7 emu.K/mol which agrees with the value for five uncoupled Ni(II) (S = 1) centers with g = 2.13.” Discuss why there are two unpaired electrons in this complex when most square-planar Ni(II) complexes are diamagnetic. A molecular orbital diagram for an octahedral metal complex would certainly help answer this question – assuming that you know how to interpret it. You can “buy” an octahedral d⁶ MO diagram from me for 5 points.
Fine-Tuning the Ring-Size of Metallacyclophanes: A Rational Approach to Molecular Pentagons

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Received August 9, 2000

The essence of supramolecular chemistry is the self-assembly of noncovalently linked molecular clusters and networks, a spontaneous process that involves various driving forces (e.g., metal–ligand interactions, ion templation, hydrogen bonding, π stacking) and chemical flexibility (i.e., facile rearrangement of the building blocks).1 In principle, if one can identify the dominant factors in a self-assembly process, they can be systematically varied to favor specific supramolecular entities. This principle is nicely illustrated by the self-assembly reactions of metal cations with bis-chelating ligands such as bptz.2-4 Among our early findings in this chemistry was that the molecular squares [M4(bptz)4(MeCN)8][ClO4]2 (M: Ni, Zn) form in high yields with [BF4]- and [ClO4]- but not with anions such as [PF6]-, [BPh4]-, and [CF3SO3]-. Armed with this information, we launched a comprehensive investigation into the role of the anion in determining the products of metal/bptz reactions. The premise of the studies was that other nuclearities could be favored, provided the appropriate anion is available to act as a template. If one considers the size and shape parameters of common anions,5 [BF4]- with Vm = 63 Å3 compared to 38 and 47 Å3 for [BF4]- and [ClO4]-, respectively, is an excellent candidate for the formation of a slightly larger cyclic entity. On the basis of this premise, [Ni(CH3CN)6][SbF6]2 was reacted with bptz in a 1:1 ratio in acetonitrile (Scheme 1).

The reaction mixture converts from the pale blue color of the Ni precursor to a brownish-green color within minutes. Crystals of the product were obtained in 60 to 70% yields by layering the nickelate to a brownish-green color within minutes. Crystals of the product were obtained in 60 to 70% yields by layering the reaction solution with toluene. An X-ray crystallographic study identified the new compound as [Ni(bptz)2(CH3CN)3][SbF6] [I] (1) which contains a novel molecular pentagon whose asymmetric unit is shown in Figure 1.7 As found for [M4(bptz)4(CH3CN)4][X]19 (M: Ni2+, Zn2+; X: [BF4]-, [ClO4]-), the cavity of [I] is occupied by an anion, in this case [SbF6]2-. (Figure 2). The six-coordinate Ni2+ ions are coordinated to two cis bptz ligands and two CH3CN molecules. It is interesting to note that, although an ideal pentagon requires 108° vertices, the angles subtended by the N–N–N edges are much smaller, for example, N(4)–Ni(1)–N(7) = 92.1-°. The problem of forming a pentagon from 90° disposed

Figure 1. ORTEP drawing of the asymmetric unit of [I] in [I][SbF6]2·2CH3CN. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angels (deg): Ni(1)–N(3) 2.055-(12), Ni(1)–N(4) 2.072(10), Ni(1)–N(17) 2.048(13), N(4)–Ni(1)–N(3) 78.6(4), N(4)–Ni(1)–N(7) 92.1(4), N(17)–Ni(1)–N(16) 91.6(5).

(a) 

(b) 

Figure 2. (a) ORTEP drawing of the molecular structure of the [I] ion. Thermal ellipsoids are drawn at the 50% probability level and (b) space-filling diagram of the molecular cation with the encapsulated [SbF6]2- ion.

Chart 1

\[
\text{Scheme 1}
\]

\[
\text{Ni}[\text{CH3CN}\text{]}\text{6}[\text{SbF6}2] + \text{Bptz} \rightarrow \text{Ni}5[\text{bptz}3][\text{CH3CN}10][\text{SbF6}10]
\]

published 01/06/2001

10.1021/ja002960r CCC: $20.00 © 2001 American Chemical Society
L–M–L building blocks, however, is solved by the flexibility of the bptz edges which adopt ~8.4° dihedral angles between the pyridyl and the tetrazine rings (Figure 3). This situation leads to overall angles between the Ni vertices of 92.1° + (2 × 8.4°) = 108.9° which is nearly ideal for a five-membered ring.

The role of the anion in dictating the outcome of self-assembly reactions has only recently become a focus of major attention in the literature.8 In addition to the identity of the anion, the choice of metal ion is also crucial to the outcome of these reactions. In the present chemistry, labile metal ions such as Ni(II) or Zn(II) lead to high yields of crystalline product with bptz, presumably because their weaker M–N interactions permit self-reorganization, thereby reducing the likelihood of obtaining insoluble kinetic products. The persistence of the pentagon unit in solution was demonstrated by electrospray ionization mass spectrometric studies.9 The isotope clusters found at m/z 3114.34, 3349.24 and 3584.13 correspond to the +1 charged cationic species: [Ni_bptz(SbF_6)_3]^+, [Ni_bptz(SbF_6)_2]^2+ and [Ni_bptz(SbF_6)_3]^+. Electrochemical and optical studies also support the conclusion that the pentagon remains intact in solution and does not revert to a mixture of species.10

Magnetic susceptibility measurements were performed on a polycrystalline sample (27.84 mg) of [I][SbF_6]_10 in the temperature range of 1.8–300 K (Figure 4). Above 50 K, χT is constant at ~5.7 emu K/mol which agrees with the value for five uncoupled Ni(II) (S = 1) centers with g = 2.13. Below 50 K, χT gradually decreases until ~10 K and then rapidly decreases to a value of 2.38 emu K/mol at 1.8 K. A model of the magnetic behavior that takes into account only zero-field splitting effects 11 does not give a satisfactory fitting (Figure 4), as ΔB is relatively high (10 K).12 The introduction of antiferromagnetic exchange13 allows one to obtain a good fitting of the experimental data (Figure 4) with g = 2.16, ΔB = +4.9 K and zJkB = -1.4 K.11 As previously noted for [Ni_bptz(C_6H_5CN)_5]^4+, superexchange through the bptz ligands is quite weak.4

As far as we are aware [Ni_bptz(CH_3CN)_10]^10+ is only the second example of a metalappentagon to be structurally characterized.36,37 The fact that the reaction between Ni(II) and bptz can be tuned by the choice of counterion to favor molecular pentagons over molecular squares is compelling evidence for an exquisite anion template effect in this chemistry. The choice of [SbF_6]^- in this study was based on the fact that its shape and size render it an excellent prospect for occupying a cavity slightly larger than that of the square, viz., a pentagon. Electrospray mass spectrometric results indicate that the squares and pentagons are not interconverting in solution to form an equilibrium mixture. It is interesting to note, however, that complete conversion of the pentagon to the square or vice versa can be effected by adding an excess amount of the anion that stabilizes the other cavity size.15 Details of these studies and related reactions of Mn(II), Co(II), and Zn(II) with bptz are contained in a full paper that is in progress.

Acknowledgment. K.R.D. gratefully acknowledges the National Science Foundation for support of this work (NSF CHE-9906583, CHE-9807975, NSF-9974899). We also acknowledge Dr. J. H. Reibenspies for assistance with X-ray crystallographic refinement. D.H.R. and J.M.K. thank the NSF (CHE-9629966) and the U.S. Department of Energy (Division of Chemical Science, O.E.B.S.).

Supporting Information Available: Crystallographic data for [I][SbF_6]_10 and the molecular squares in ref 5 (crystallographic information, atomic coordinates, bond lengths and angles, and structure factors) and ESIMS mass spectra for [I][SbF_6]_10 (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

JA002960R


(9) Positive ion electrospray mass spectra were acquired in acetoniitrile using a SCIEX QStar Pulsar with a Protana Nanospray ion source. Data were acquired with TOFMA 2.0RC3 and analyzed with BioMultiView 1.5RC3.

(10) Cyclic voltammetric studies in CH_3CN: Eccoli (red) = +0.28 V (quasi-reversible) and Eccoli (p.e.) = -1.26 V, UV-vis = 510 nm (ε = 540 M^-1 cm^-1) and 690 nm (ε = 260 M^-1 cm^-1). These data reveal an absence of free ligand and a mixture of fragments that would result from decomposition.


\[ \chi_T = \frac{2N_g\mu_B^2}{3k_B T} \left( c^{-1} + 2x(1 - c^{-1}) \right) \]

where \( x = \Delta B/k_BT \) is the zero-field splitting parameter.

(13) Since magnetic interactions through bptz ligands are smaller than the ZFS (D) of the Ni(II),4 the mean field approximation was used.11


(15) Specifically, if [Ni_bptz(CH_3CN)_10][SbF_6]_10 is dissolved in CH_3CN and treated with an excess of [BF_4]^- , complete conversion to [Ni_bptz(CH_3CN)]^10+ occurs as determined by ES-MS as well as single-crystal X-ray crystallography.