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Fine-Tuning the Ring-Size of Metallacyclophanes: A Rational Approach to Molecular Pentagons

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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, (3,6-bis(2-pyridyl)1,2,4,5-tetrazine).[2−4] Among our early findings in this chemistry was that the molecular squares $[M_4(bptz)_4(MeCN)_8]^{8+}$ (M: Ni, Zn)[4,5] form in high yields with $[BF_4]^-$ and $[ClO_4]^-$ but not with anions such as $[PF_6]^-$, $[BPh_4]^-$, and $[CF_3SO_3]^-$. 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,[6] $[SbF_6]^-$ with $V_m = 63$ Å^3 compared to 38 and 47 Å^3 for $[BF_4]^-$ and $[ClO_4]^-$, respectively, is an excellent candidate for the formation of a slightly larger cyclic entity. On the basis of this premise, $[Ni(CH_3CN)_6][SbF_6]_2$ 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 reaction solution with toluene.

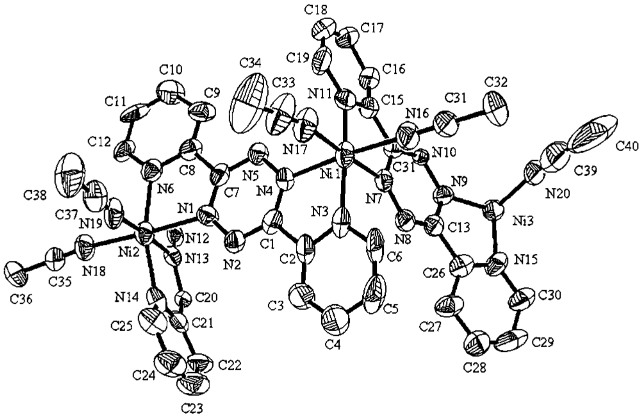


Figure 1. ORTEP drawing of the asymmetric unit of $[\mathbf{1}]^{10+}$ in $[\mathbf{1}][SbF_6]_{10}\cdot 2CH_3CN$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ni(1)−N(3) 2.055(12), Ni(1)−N(4) 2.072(10), Ni(1)−N(17) 2.048(13), N(4)−Ni(1)−N(3) 78.6(4), N(4)−Ni(1)−N(7) 92.1(4), N(17)−Ni(1)−N(16) 91.6(5).

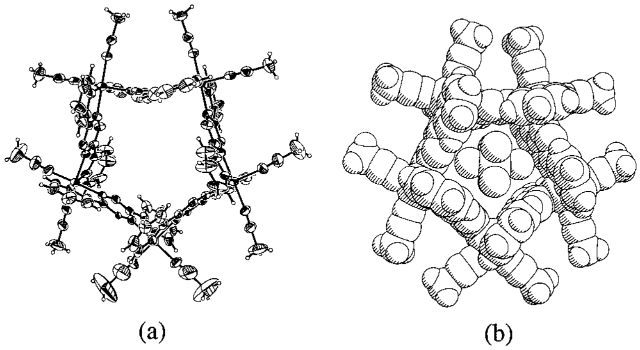
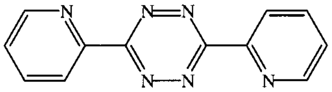


Figure 2. (a) ORTEP drawing of the molecular structure of the $[\mathbf{1}]^{10+}$ ion. Thermal ellipsoids are drawn at the 50% probability level and (b) space-filling diagram of the molecular cation with the encapsulated $[SbF_6]^-$ ion.

Chart 1



Scheme 1

$$5[Ni(CH_3CN)_6][SbF_6]_2 + 5bptz \xrightarrow[RT]{CH_3CN} [Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$$

An X-ray crystallographic study identified the new compound as $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ ($[\mathbf{1}][SbF_6]_{10}$) which contains a novel molecular pentagon whose asymmetric unit is shown in Figure 1.[7] As found for $[M_4(bptz)_4(CH_3CN)_8][X]_8$, (M: Ni^{2+}, Zn^{2+}; X: $[BF_4]^-$, $[ClO_4]^-$), the cavity of $[\mathbf{1}]^{10+}$ is occupied by an anion, in this case $[SbF_6]^-$ (Figure 2). The six-coordinate Ni^{2+} ions are coordinated to two *cis* bptz ligands and two CH_3CN molecules. It is interesting to note that, although an ideal pentagon requires 108° vertices, the angles subtended by the N−Ni−N edges are much smaller, for example, N(4)−Ni(1)−N(7) = 92.1(4)°. The problem of forming a pentagon from 90° diposed

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(5) Campos-Fernández, C. S.; Clérac, R.; Dunbar, K. R. Manuscript in preparation. Analogous reactions of $[Zn(CH_3CN)_4][BF_4]_2$, $[Zn(H_2O)_6][ClO_4]_2$, and $[Ni(H_2O)_6][ClO_4]_2$ with bptz have been performed. In all cases the molecular squares were isolated. (a) $[Zn_4(bptz)_4(CH_3CN)_8][BF_4]_8\cdot 4CH_3CN$ at 110(2) K: $C_{72}H_{68}B_8F_{32}N_{36}Zn_4$, $M_r = 2393.6$, *P*-1, $a = 13.924$ (5) Å, $b = 17.071(5)$ Å, $c = 21.940(5)$ Å, $\alpha = 94.458(5)°$, $\beta = 92.510(5)°$, $\gamma = 97.790(5)°$, $V = 5144$ Å^3, $Z = 2$, R1(wR2) = 0.0695(0.2017), GOF = 1.035, F^2 refinement in SHELXTL 5.0. (b) $[Zn_4(bptz)_4(CH_3CN)_8][ClO_4]_8\cdot 3CH_3CN$ at 110(2) K: $C_{70}H_{65}Cl_8N_{35}O_{32}Zn_4$, $M_r = 2453.7$, *C*2/*c*, $a = 20.377(4)$Å, $b = 16.634(3)$Å, $c = 28.283(6)$ Å, $\beta = 102.30°$, $V = 9366$ Å^3, $Z = 4$, R1(wR2) = 0.0774(0.2244), GOF = 1.035, F^2 refinement in SHELXTL 5.0. (c) $[Ni_4(bptz)_4(CH_3CN)_8][ClO_4]_8\cdot 3CH_3CN\cdot C_4H_8O$ at 110(2) K: $C_{74}H_{73}Cl_8N_{36}O_{33}Ni_4$, $M_r = 2499.0$, $P2_1/n$, $a = 15.082$ (3) Å, $b = 31.922(6)$ Å, $c = 22.305(5)$ Å, $\beta = 104.11(3)°$, $V = 10415$ Å, $Z = 4$, R1(wR2) = 0.0641(0.1584), GOF = 0.889, F^2 refinement in SHELXTL 5.0.

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(7) Crystal data for $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}\cdot 2CH_3CN$, $[\mathbf{1}][SbF_6]_{10}\cdot 2CH_3CN$ at 110(2) K: $C_{84}H_{76}F_{60}N_{42}Sb_{10}Ni_5$, $M_r = 4324.7$, dark-brown rectangles, $0.13 \times 0.2 \times 0.05$ mm^3, *C*2/*c*, $a = 17.933(4)$ Å, $b = 28.314(6)$ Å, $c = 29.459(6)$ Å, $\beta = 104.82°$, $V = 14460$ Å^3, $Z = 4$, $\rho_{calc} = 1.916$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 2.121$ mm^{-1}. Data were collected on a Bruker CCD SMART system in the range $4 < 2\theta < 49°$. A total of 36 580 measured reflections, 12 327 unique, 8016 with $F_o^2 \geq 4\sigma(F_o^2)$ were used to refine 891 parameters to R1(wR2) = 0.1160(0.33645), GOF = 1.069, F^2 refinement in SHELXTL-5.0. Four out of the 10 $[SbF_6^-]$ ions were highly disordered, which accounts for higher than usual *R* factors.

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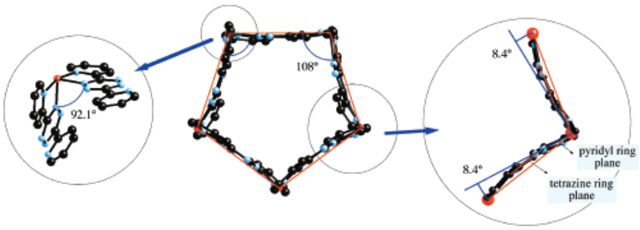

Figure 3. A skeletal view of the $Ni_5(bptz)_5$ pentagon superimposed on an ideal pentagon to emphasize the distortion of the ligands.

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 $92.1° + (2 \times 8.4°) = 108.9°$ 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: $[Ni_5(bptz)_5(SbF_6)_7]^+$, $[Ni_5(bptz)_5(SbF_6)_8]^+$, and $[Ni_5(bptz)_5(SbF_6)_9]^+$, respectively. 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 $[\mathbf{1}][SbF_6]_{10}$ 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 D/k_B is relatively high (10 K).[12] The introduction of antiferromagnetic exchange[13] allows one to obtain a good fitting of the experimental data (Figure 4) with $g = 2.16$, $D/k_B = +4.9$ K and $zJ/k_B = -1.4$ K.[11] As previously noted for $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$, superexchange through the bptz ligands is quite weak.[4]

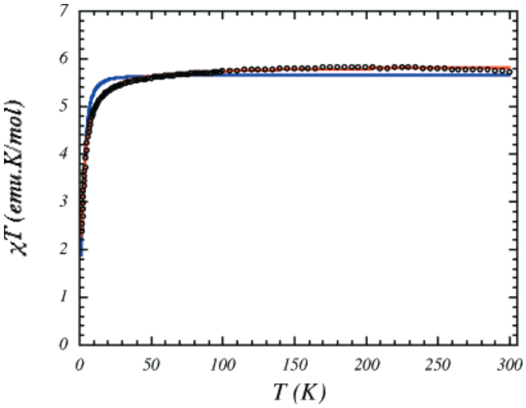

Figure 4. Temperature dependence of the χT product at 1000 G for $[\mathbf{1}][SbF_6]_{10}$. The solid lines are the fitting obtained by considering only the zero-field splitting (blue) and by taking into account both zero-field splitting and antiferromagnetic interactions in the theoretical model (red). Magnetic susceptibility data were corrected for diamagnetic contribution calculated from Pascal's constants.[14]

As far as we are aware $[Ni_5(bptz)_5(CH_3CN)_{10}]^{10+}$ is only the second example of a metallapentagon to be structurally characterized.[8a,c] The fact that the reaction between Ni^{2+} ions 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.

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Supporting Information Available: Crystallographic data for $[\mathbf{1}][SbF_6]_{10}$ and the molecular squares in ref 5 (crystallographic information, atomic coordinates, bond lengths and angles, and structure factors) and ESI-MS mass spectra for $[\mathbf{1}][SbF_6]_{10}$ (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via Internet at http://pubs.acs.org.

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(9) Positive ion electrospray mass spectra were acquired in acetonitrile 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: $E_{1/2}(\text{red}) = +0.28$ V (quasi-reversible) and $E(\text{p,c}) = -1.26$ V. UV−vis spectra: 510 nm ($\epsilon = 540$ M^{-1} cm^{-1}) and 690 nm ($\epsilon = 260$ M^{-1} cm^{-1}). These data reveal an absence of free ligand and a mixture of fragments that would result from decomposition.

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(12) The χT expression used for fitting is:

$$\chi_{ZFS}T = \frac{2Ng^2\mu_B}{3k_BT}\left[\frac{e^{-x} + 2/x(1 - e^{-x})}{(1 - e^{-2x})}\right]$$

where $x = D/k_BT$, D 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]

$$\chi T = \frac{\chi_{ZFS}T}{1 - \left(\frac{2zJ}{Ng^2\mu^2_B}\right)\chi_{ZFS}}$$

Here z is the number of next neighbors, and J is the magnitude of the magnetic interactions.

(14) *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; John Wiley and Sons: New York, 1976.

(15) Specifically, if $[Ni_5(bptz)_5(CH_3CN)_{10}][SbF_6]_{10}$ is dissolved in CH_3CN and treated with an excess of $[BF_4]^-$, complete conversion to $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ occurs as determined by ES-MS as well as single-crystal X-ray crystallography.