gave the specific rotations in the ORD at the recorded wavelengths (Table 1). As the calculated data are for the gas phase, whereas the experimental ones are obtained for solutions, the computed values are systematically somewhat too large. Nevertheless, the agreement between experiment and theory is remarkably good and emphasizes the quality of the theoretical approach used here.[29]

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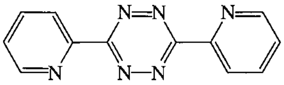
A One-Pot, High-Yield Synthesis of a Paramagnetic Nickel Square from Divergent Precursors by Anion Template Assembly**

Cristian S. Campos-Fernández, Rodolphe Clérac, and Kim R. Dunbar*

Self-assembly of metal cations with nitrogen heterocyclic bridging ligands is a central theme in supramolecular chemistry aimed at developing light-harvesting assemblies of electronically coupled metal centers.[1] The ability of these π-ligand systems to transmit electronic information between remote metal centers is well-documented,[1–4] but much less is known about their suitability for promoting strong superexchange between paramagnetic centers. The bis-chelating α-diimine ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) with its low-lying π* orbitals is a particularly promising candidate for use as an electronic spacer,[5] as judged by the strong coupling observed between the metal centers in $[(NH_3)_4Ru(\mu\text{-bptz})Ru(NH_3)_4]^{4+}$ which exhibits a K_c value of 10^{15}.[5f]



bptz

Studies in our laboratories have revealed a new application for the bptz molecule, namely as a linking group in the formation of paramagnetic squares. The bptz ligand is ideally suited for this purpose for two reasons. First bptz is a rigid molecule with two bipyridine units on each end suitable for bridging two metals, and second two bptz ligands coordinated to an octahedral metal center are required to be *cis* to each other. These binding preferences are being capitalized upon in one-pot, high-yield reactions of unprotected solvated cations $[M(CH_3CN)_6]^{2+}$ with bptz in the presence of tetrafluoroborate anions. In this study we report an unusual, high-yield formation of a cyclic product from solutions of $[Ni(CH_3CN)_6][BF_4]_2$ and bptz in a 1:1 molar ratio [Eq. (1)].[6]

$$[Ni(CH_3CN)_6][BF_4]_2 + \text{bptz} \xrightarrow[\text{RT}]{\text{MeOH}} [Ni_4(\text{bptz})_4(CH_3CN)_8][BF_4]_8 \qquad (1)$$

Regardless of the ratio of bptz and $[Ni(CH_3CN_6)][BF_4]_2$, the reactions proceed at room temperature in MeOH to give a dark green solution with eventual deposition of a green solid (74 % yield). Single crystals of the product are easily obtained by diffusion of toluene into a solution of the compound in acetonitrile. The reactions are quite remarkable in that there is no evidence for polymer formation in spite of the lack of protective groups and the relatively high concentrations used for the reaction. Hupp and co-workers have reported similar observations for various octahedral based squares prepared under refluxing conditions in their laboratories, and it is clear from their detailed analyses that cyclic oligomers are thermodynamic products.[7]

An X-ray crystallographic study revealed the new compound to be the partially solvated molecular square $[Ni_4(\text{bptz})_4(CH_3CN)_8][BF_4]_8 \cdot 4\,CH_3CN$.[8] An ORTEP diagram is provided in Figure 1 (top) and a packing diagram is

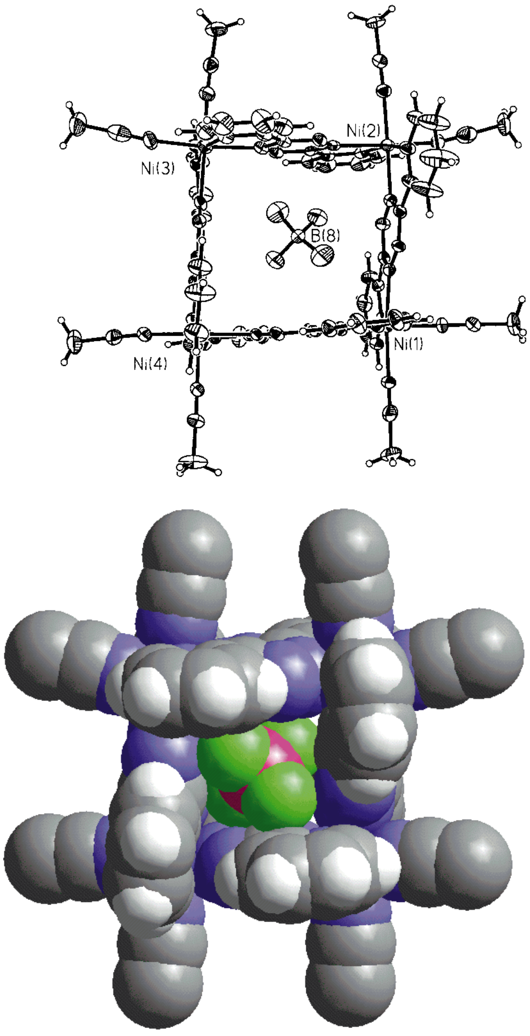


Figure 1. Top: ORTEP drawing of the molecular structure of the $[Ni_4(\text{bptz})_4(CH_3CN)_8]^{8+}$ ion. Thermal ellipsoids are drawn at the 50 % probability level; bottom: space-filling diagram of the molecular cation with the encapsulated $[BF_4]^-$ ion.

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provided in Figure 2. The coordination geometries of the Ni^{II} ions are octahedral as expected, with four of the coordination sites being occupied by two different bptz chelate donors and the other two positions being capped by CH_3CN molecules.

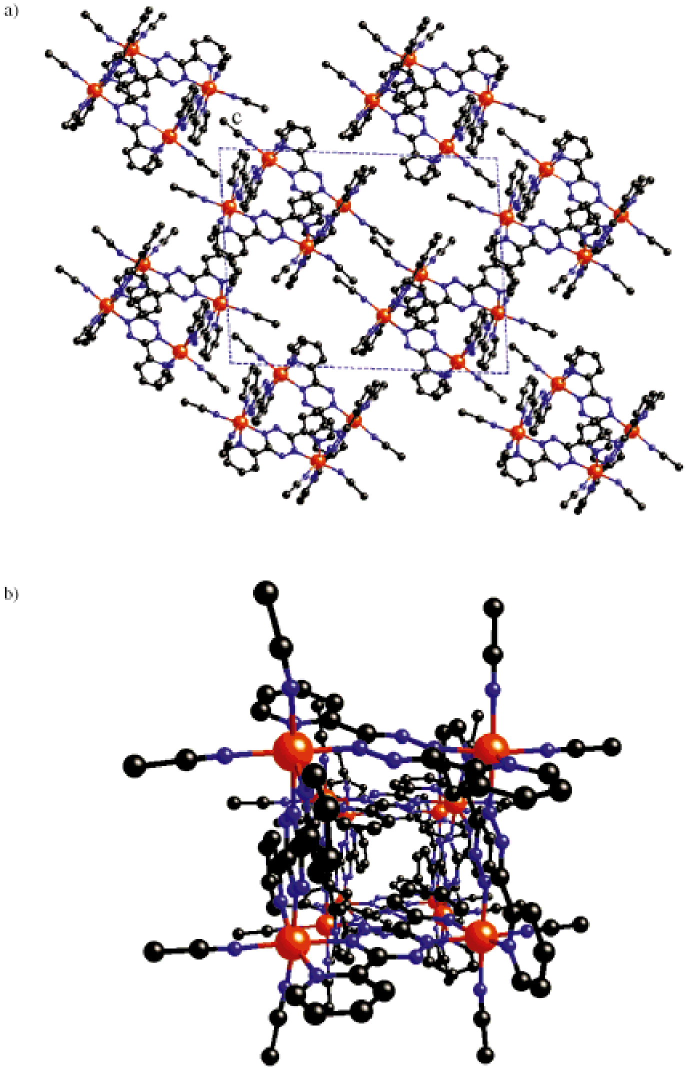

Figure 2. Packing arrangement of the Ni_4 cations emphasizing the a) and b) side views of the stacks.

The void space in the center of the square is about 4.6 Å in diameter which is an excellent size match for the $[BF_4]^-$ ion that resides in this cavity (Figure 1 bottom). The encapsulated anion appears to be central to the formation of the cyclic oligomer as evidenced by the fact that products with other anions are of a different color than the $[BF_4]^-$ salt and are noncrystalline. For example, $[Ni(CH_3CN)_6][PF_6]_2$ reacts with bptz in MeOH to give dark orange-brown solutions from which only powders can be isolated. Anion template reactions are of considerable current interest in the self-assembly of supramolecular structures,[9] but compared to cation-assisted processes, they are much less prevalent. A particularly relevant example to the present work is the report of a $[BF_4]^-$-templated synthesis of a $[Co_4]^{8+}$ cage molecule which retains an encapsulated anion in solution.[9h] The authors used a combination of mass spectrometry and NMR spectroscopy to support the conclusion that the anion assists in the assembly of the tetrameric unit. These approaches were also used to lend insight into the possible role of the anion in the synthesis of $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8$, but NMR spectroscopy revealed only one broad ^{11}B and ^{19}F resonance. This may be due to the paramagnetism of the molecule or to rapid exchange of the encapsulated $[BF_4]^-$ ion with the outer-sphere anions, although the latter is unlikely since low-temperature NMR measurements did not produce any changes in the spectra. The most convincing evidence for the role of the anion comes from a FAB mass spectrometric analysis of solutions of Ni ions with bptz in the presence of various anions. Solutions containing the $[BF_4]^-$ ion give a mass cluster corresponding to the square unit, but those containing $[PF_6]^-$, $[SbF_6]^-$, or $[CF_3SO_3]^-$ show only dimeric units. We take these results as a positive indication that the anion acts as a template in the self-assembly process.

The six-coordinate geometry about the metal ions is important to our goal of obtaining magnetic squares, as a square-planar geometry leads to low-spin, primarily diamagnetic ground states.[10] Magnetic susceptibility measurements were performed on the Ni_4 compound, and, as the plot in Figure 3 indicates, μ_{eff} is constant at 5.66 μ_B between room temperature and 50 K. These data are consistent with four high-spin Ni^{II} ($S=1$) centers. Below 50 K the moment decreases which can be attributed to a zero-field splitting effect or weak antiferromagnetic interactions ($J\approx-2$ K).

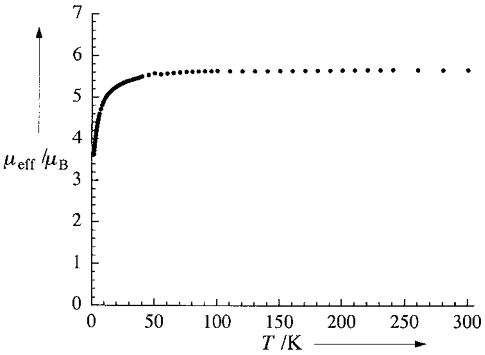

Figure 3. Thermal dependence of the effective moment at 1000 G for $[Ni_4(bptz)_4(CH_3CN)_8][BF_4]_8\cdot 4CH_3CN$.

The new Ni_4 molecule is an unprecedented type of a partially solvated molecular square, and it is the first compound of the bptz ligand to be structurally characterized. As far as we are aware, this is the first report of a molecular square formed around an encapsulated anion, and one of the few X-ray structures obtained for a square with octahedral metal ion constituents.[7, 11, 12] The only paramagnetic octahedral-based example of which we are aware is a Co^{II} [2 × 2] grid with bis-terpyridine type ligands.[12a] Five-coordinate paramagnetic Cu^{II} [2 × 2] grids with bridging pyrazole ligands have also been recently reported.[12b] The presence of the labile CH_3CN ligands in $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ render these clusters ideal building blocks for the elaboration of two-dimensional square grids. In this manner a higher order supramolecular structure can easily be envisioned as resulting from connecting the squares with linear bidentate bridges such as 4,4-bipyridine or pyrazine or even bis-chelating bidentate ligands such as bipyrimidine or oxalate. Although the unpaired electrons on the Ni^{II} ions are not magnetically communicating through the bptz ligand, this does not rule out the possibility that metal ions with different magnetic orbitals will experience superexchange. Moreover, ligand-based reduction of the π* orbitals of the bptz ligands to produce bptz radicals, which has been achieved in other metal complexes of bptz,[13] is expected to add an extra level of complexity to the magnetic properties.

Experimental Section

$[Ni(CH_3CN)_6][BF_4]_2$ (100 mg, 209 mmol) was dissolved in methanol (10 mL) and treated with bptz (47 mg, 200 mmol) under anaerobic conditions. Over the course of 5 h, the solution slowly changed color from pale red to a dark green. The solution was allowed to stir overnight during which time a green powder deposited on the bottom of the flask. The powder was dissolved in acetonitrile under anaerobic conditions and layered with toluene to give crystals of $[Ni_4(C_{12}N_6H_8)_4(CH_3CN)_8][BF_4]_8 \cdot 4\,CH_3CN$ within three days; yield: 88 mg (74%).

Magnetic susceptibility measurements were performed on a polycrystalline sample (18.8 mg) with a Quantum Design MPMS-2 SQUID magnetometer operating in the range 1.7–300 K at 1000 G.

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[6] Analogous reactions of other solvated metal ions with bptz have been performed; in the case of the $[Co(CH_3CN)_6][PF_6]_2$ precursor an unexpected result was obtained, namely the formation of the mononuclear complex $[Co(bpod)_2]^{2+}$ that contains the transformed ligand 2,5-(2-pyridyl)-1,3,4-oxadiazole (bpod).[5a] This molecule is known to be easily accessed from bptz at lower pH values, a fact that needs to be taken into account in chemistry of the bptz ligand.

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[8] Crystal data for $[Ni_4(bptz)_4(MeCN)_8][BF_4]_8 \cdot 4\,CH_3CN$ at 173(2) K: $C_{72}H_{68}N_{36}B_8F_{32}Ni_4$, $M_r = 2366.94$, light green rectangles, $0.05 \times 0.12 \times 0.25\ mm^3$, triclinic, space group $P\bar{1}$, $a = 14.118(3)$, $b = 17.090(3)$, $c = 21.774(4)$ Å, $\alpha = 94.87(3)$, $\beta = 91.43(3)$, $\gamma = 97.47(3)°$, $V = 5186.6$ Å^3, $Z = 2$, $\rho_{calcd} = 1.516\ g\,cm^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.831\ mm^{-1}$. Data were collected on a Bruker CCD SMART system in the range $4 < 2\theta < 49°$. A total of 24786 measured reflections, 16456 unique, 9444 with $F_o^2 \geq 4\sigma(F_o^2)$ were used to refine 1554 parameters to $R1(wR2) = 0.0831(0.1957)$, GOF = 1.026, F^2 refinement in SHELXTL-5.0. A ψ scan absorption correction gave min and max transmission factors of 0.88 and 0.96. The highest peak in the final difference map = 1.18 e Å^{-3}. Five out of the eight $[BF_4]^-$ ions were disordered, therefore they were each modeled in several orientations. The extensive disorder accounts for the slightly higher than usual R factors. 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-117912. 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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