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Communication

A Schiff Base Expanded Porphyrin Macrocycle that Acts as a Versatile Binucleating Ligand for Late First-Row Transition Metals

Jonathan L. Sessler,[*,†] Elisa Tomat,[†] Tarak D. Mody,[†,‡] Vincent M. Lynch,[†] Jacqueline M. Veauthier,[†] Utkir Mirsaidov,[§] and John T. Markert[§]

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165, and Department of Physics, The University of Texas at Austin, 1 University Station C1600, Austin, Texas 78712-0264

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The coordination chemistry of the Schiff base polypyrrolic octaaza macrocycle **1** toward late first-row transition metals was investigated. Binuclear complexes with the divalent cations Ni(II), Cu(II), and Zn(II) and with the monovalent cation Cu(I) were prepared and characterized. Air oxidation of the Cu(I) ions in the latter complex to their divalent oxidation state resulted in a change in the coordination mode relative to the macrocycle.

The expanded porphyrin Schiff base macrocycle **1** was synthesized in our laboratories in the early 1990s. Its binding of methanol both in solution and in the solid state provided the first example of neutral substrate complexation with an expanded porphyrin.[1] Although not reported at that time, the large octaaza framework of macrocycle **1**, featuring both pyrrolic and iminic nitrogens, makes it appealing as a potential cation-complexing ligand capable of stabilizing binuclear metal complexes.[2]

A considerable effort has been devoted in recent years to the preparation of binuclear complexes of expanded porphyrins.[3−14] The fast-growing interest in this field reflects a confluence of several factors. First, several polypyrrolic macrocycles have been found to act as ligands for a range of larger cations, which has led to the consideration that more than a single metal center could be coordinated in an appropriate system. Second, in contrast to the relatively rigid scaffold provided by porphyrin and related tetrapyrrolic macrocycles, the size and functionality of expanded porphyrins can potentially be varied to allow access to a larger number of coordination modes. Third, the preorganization of two or more metals centers at short separations (2.5−6.0 Å) would pave the way to studies involving cooperativity in catalysis and enzyme mimicking. Given the number of expanded porphyrin macrocycles prepared to date and the relatively small number of well-characterized metal complexes that have been reported, it is clear that many aspects of expanded porphyrin coordination chemistry remain to be explored. This is clearly true in the case of **1**.

In this communication, we describe the synthesis and characterization of binuclear Ni(II), Cu(I), Cu(II), and Zn(II) complexes of ligand **1**. Additionally, we report a change in coordination mode observed after oxidation of the Cu(I) complex to form a bis-Cu(II) species.

The free base form of macrocycle **1** was obtained by adding Et_3N to a suspension of the diprotonated nitrate salt

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[*] To whom correspondence should be addressed. E-mail: sessler@mail.utexas.edu.

[†] Department of Chemistry.

[‡] Current address: Pharmacyclics, Inc., 995 East Arques Avenue, Sunnyvale, CA 94085.

[§] Department of Physics.

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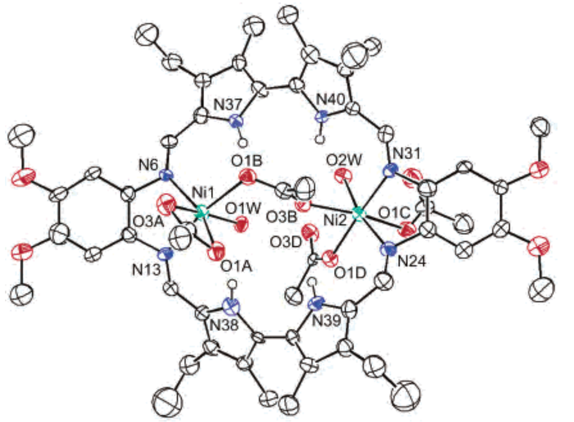
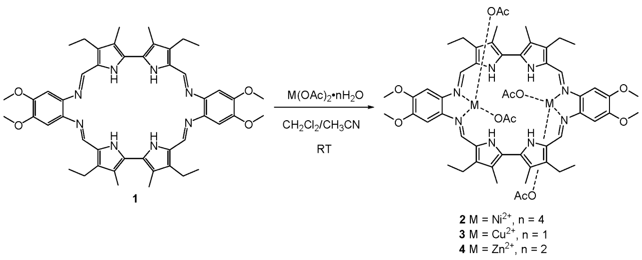


Figure 1. Top view of the bis-Ni(II) complex **2** showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. Selected bond distances (Å): Ni1−O1W 2.027(7), Ni1−O1B 2.131(8), Ni1−O1A 2.211(8), Ni1−O3A 2.056(8), Ni1−N6 2.050(9), Ni1−N13 2.053(9), Ni2−O2W 2.119(7), Ni2−O3B 2.085(8), Ni2−O1D 2.035(8), Ni2−O1C 2.033(7), Ni2−N24 2.137(10), Ni2−N31 2.078(10). Ni1···Ni2 5.375 Å.

Scheme 1



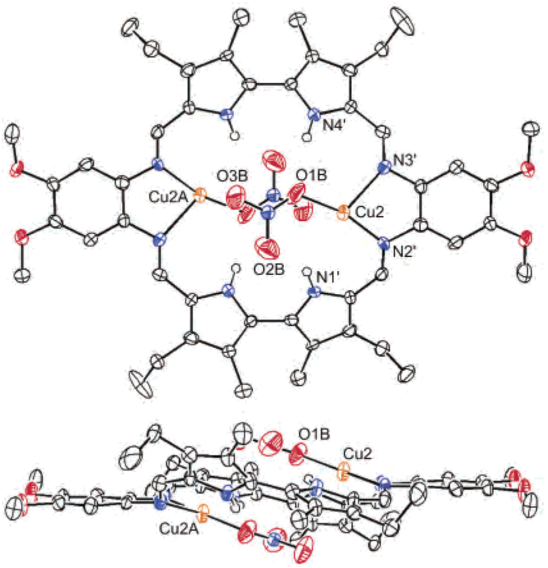
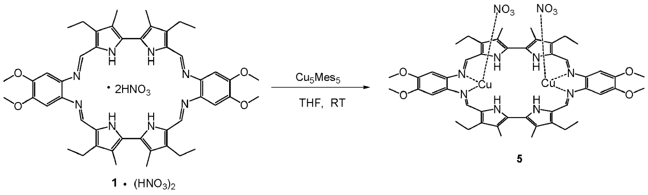


Figure 2. Top and side views of the bis-Cu(I) complex **5** showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. The macrocycle lies around a crystallographic inversion center at 1, $^{1}/_{2}$, $^{1}/_{2}$. Except for the copper atom Cu2A, atoms related by the inversion center are not labeled. Selected bond distances (Å) and angles (deg): Cu2−O1B 1.917(3), Cu2−N2′ 1.944(4), Cu2−N3′ 2.116(4), O1B−Cu2−N2′ 165.80(18), O1B−Cu2−N3′ 109.65(17), N2′−Cu2−N3′ 84.50(17). Cu2···Cu2A 5.296 Å.

Scheme 2



1·$(HNO_3)_2$ in CH_2Cl_2. Alternatively, this form could be obtained by washing this same suspension in CH_2Cl_2 with a saturated aqueous solution of $NaHCO_3$. Subsequent addition of nickel(II), copper(II), or zinc(II) acetate salts (Scheme 1) at room temperature gave complexes **2**−**4**.

These complexes were characterized through high-resolution mass spectrometry and elemental analysis; solid-state structural information for the bis-Ni(II) complex **2** was obtained from a single-crystal X-ray diffraction analysis (Figure 1).

As can be seen from an inspection of Figure 1, the two Ni(II) ions lie in a distorted octahedral geometry and are coordinated to the macrocycle by the iminic nitrogens. Interestingly, the pyrrolic nitrogens do not participate in metal complexation. The hydrogen atoms of the bypyrrolic nitrogens are hydrogen-bound to the donor oxygens of the four acetate counterions. The acetate ions also coordinate to the Ni(II) centers and do so in three distinct binding modes. First, a bidentate acetate group coordinates to Ni1 through donor atoms O1A and O3A. Second, a bridging acetate group binds to Ni1 and Ni2 through atoms O1B and O3B, respectively. Finally, two monodentate acetates bind to Ni2. Each Ni(II) ion is also coordinated to a water molecule. The Ni−Ni distance in the complex is 5.375 Å.

The ability of macrocycle **1** to coordinate readily nickel, copper, and zinc in their divalent oxidation states prompted us to explore whether this ligand could form complexes with a typical monovalent metal cation, namely, Cu(I).[15] Toward this end, the diprotonated nitrate salt **1**·$(HNO_3)_2$ was reacted with the mesitylene Cu(I) reagent Cu_5Mes_5[16] in THF at room temperature under argon (Scheme 2). Initial mass spectrometric data indicated the formation of a binuclear copper complex but did not provide interpretable information about the oxidation state of the metal ions. The formation of the bis-Cu(I) complex (**5**), as opposed to a bis-Cu(II) or mixed-valent species, was first inferred from ^1H NMR spectroscopic measurements (see Supporting Information) and subsequently confirmed by X-ray diffraction analysis (Figure 2).

In complex **5**, the macrocycle lies around a crystallographic inversion center, and each Cu(I) ion coordinates two imine donors of the macrocycle and one oxygen of the nitrate counterion, leading to a distorted T-shaped planar arrangement of these atoms. The coordination planes, containing the Cu ions and the nitrate anions, are tilted above and below the average plane of the macrocycle such that each counterion interacts with only one metal center. The Cu(I)−Cu(I) distance is 5.296 Å.

The structures of the binuclear complexes **2** (Figure 1) and **5** (Figure 2) indicate that macrocycle **1** can support both

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(15) To date, we have obtained preliminary evidence that system **1** stabilizes the formation of complexes from several second-row transition metal cations, including Rh(I) and Ag(I).

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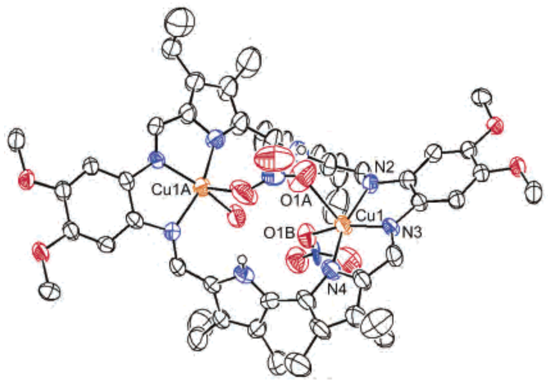
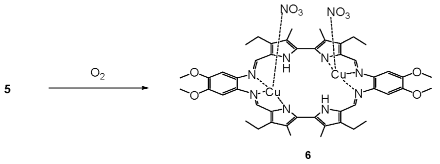


Figure 3. View of the bis-Cu(II) complex **6** showing a partial atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. Selected bond lengths (Å): Cu1−N3 1.947(4), Cu1−N4 1.956(5), Cu1−O1B 1.970(4), Cu1−N2 2.037(4), Cu1−O1A 2.430(5). Cu1···Cu1A 5.289 Å.

Scheme 3



monovalent and divalent cations in a similar coordination mode involving the imine nitrogens but not the pyrrolic nitrogens. However, this is not the only binding mode available to ligand **1**. This fact is underscored by what is observed when crystals of **5** are exposed to air, dissolved in CH_2Cl_2, and layered with *n*-pentane. The result is oxidation of the metal centers from Cu(I) to Cu(II) (Scheme 3) and the production of a new complex (**6)** as a crystalline solid that was characterized by mass spectrometry, elemental analysis, and X-ray diffraction analysis (Figure 3).

The crystal structure of **6** shows that the two additional anionic ligands, which are required by the charge balance of the complex, are provided by the macrocycle itself. Indeed, the ligand undergoes a dramatic distortion in order to coordinate to each Cu(II) ion not only via the two imine nitrogen atoms but also through a pyrrolic nitrogen. As a consequence, the metal ions lie in a distorted square-pyramidal ligand environment that includes a bridging nitrate ion. The fifth coordination site is occupied by the second nitrate counterion for Cu1 and by a water molecule for Cu1A. The Cu(II)−Cu(II) distance in **6** is 5.289 Å.

Efforts to obtain complex **6** directly by treatment of **1**·$(HNO_3)_2$ and subsequent addition of $Cu(NO_3)_2$ failed. Instead, what appears to be obtained is the analogue of **3** with four nitrates rather than four acetates. To date, this species has not been fully characterized.

As expected from the large separation between the metal centers in complexes **2**, **3**, and **6**, no evidence of a magnetic coupling was seen in solution at room temperature (Evans method).[17,18] Additionally, magnetic susceptibility SQUID data for these complexes were consistent with a paramagnetic behavior of these complexes in the temperature range (5−300 K), as would be expected in the absence of a magnetic interaction between the two Ni(II) centers in **2** and between the two Cu(II) centers in **3** and **6** (see Supporting Information).

In summary, we have shown that macrocycle **1** can act as a versatile binucleating ligand. It stabilizes the formation of binuclear complexes of several transition metals and can interact with bound cations via two different coordination modes. We thus believe that ligand **1** and its Schiff-base oligopyrrolic congeners might have an important role to play as “switchable ligands” that can adjust to accommodate changes in cation size and shape, as well as external environment. Such switchable systems could help advance the coordination chemistry of expanded porphyrins and could lead to the production of useful catalyst systems. Consistent with this suggestion, we have recently reported[4] the effect of changes in the protonation state of a Schiff base macrocycle (i.e., reaction of acid salt vs free base) on the coordination modes of binuclear μ-oxo iron complexes. In contrast to this earlier work, the change in coordination mode from complex **5** to complex **6** is related to the oxidation state of the metal ions. Taken in concert, these results illustrate the potential versatility of the generalized oligopyrrole Schiff base switchable ligand approach. Further studies of systems such as **1** are thus in progress.

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Supporting Information Available: Synthetic details for complexes **2**−**6**; X-ray structural data for **2**, **5**, and **6**; magnetic susceptibility data for **2**, **3**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The Evans method solution magnetic moments were calculated using the formula reported by Grant (see ref 17b) as corrected for high-field superconducting NMR spectrometers according to the formula of Schubert (see ref 17c). Bis-Ni(II) complex **2**: μ_{eff} ($CDCl_3$, 296 K) = (4.0 ± 0.1) μ_B. Calculated value for two independent octahedral Ni(II) centers (*high-spin* d^8, $S = 1$): 4.00 μ_B. Bis-Cu(II) complex **3**: μ_{eff} ($CDCl_3$, 296 K) = (2.5 ± 0.1) μ_B, bis-Cu(II) complex **6**: μ_{eff} ($CDCl_3$, 296 K) = (2.5 ± 0.1) μ_B. Calculated value for two independent Cu(II) centers (d^9, $S = {}^1/_2$): 2.45 μ_B.