

Binuclear Fluoro-Bridged Zinc and Cadmium Complexes of a Schiff Base Expanded Porphyrin: Fluoride Abstraction from the Tetrafluoroborate Anion

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Reactions of the Schiff base oligopyrrolic octaazamacrocyclic **1** with BF_4^- salts of divalent zinc and cadmium result in fluoride anion abstraction and the formation of difluoride-bridged metal complexes. X-ray diffraction analyses provide support for the notion that hydrogen-bonding interactions, involving the N–H groups of the macrocycle and the coordinated fluoride ions, play an important role in stabilizing these new complexes.

Because of the small size and high electronegativity of the fluorine atom, the fluoride anion was long considered a quintessential hard ligand. In accordance with such thinking, for many years it was expected that complexes with soft, low-valent transition metals would be unstable. Current research in this area,¹ encouraged by the occurrence of metal–fluoride fragments in transition-metal-mediated C–F bond activation reactions,² has shown that this traditional point of view is inadequate. Indeed, nowadays the fluoride anion is recognized as being a viable ligand for low-valent transition-metal cations.

Although the number of well-characterized fluoro complexes has grown considerably in recent years, many of them, in particular the bi- or polynuclear complexes, have been obtained as the result of serendipity.³ The eclectic manner in which most low-valent transition-metal fluoride anion

complexes have been obtained can be attributed, at least in part, to the lack of convenient methods for introducing the fluorine atom into the primary coordination sphere of such metal species.¹ Indeed, because of the poor solubility, toxicity, general sensitivity, and hygroscopic character of typical fluorinating agents (e.g., F_2 , HF, KF, XeF_2 , CoF_3 , etc.), it would be desirable to develop synthetic approaches that are more convenient and less hazardous.

The intentional decomposition of the tetrafluoroborate anion provides an elegant method for the delivery of fluoride to coordination compounds involving heterocyclic ligands.⁴ The use of metal tetrafluoroborate salts is especially convenient in this regard because it obviates the need to add a separate fluorinating agent and to remove the resulting byproducts. Recently, Reger et al. reported that binucleating ligands, which allow for the juxtaposition of coordinatively unsaturated metal centers (i.e., Fe^{II} , Zn^{II} , and Cd^{II}), can be used to effect the cooperative abstraction of fluoride from the tetrafluoroborate anion and the consequent formation of fluoro-bridged metallacyclic compounds.⁵ In this Communication, we show that this approach may be extended into the realm of expanded porphyrin chemistry. In particular, we describe the synthesis and characterization of binuclear Zn^{II} and Cd^{II} complexes of ligand **1** that feature fluoride bridges between the metal centers. These products are, to the best of our knowledge, the first examples of fluoro–metal complexes stabilized using oligopyrrolic macrocycles.

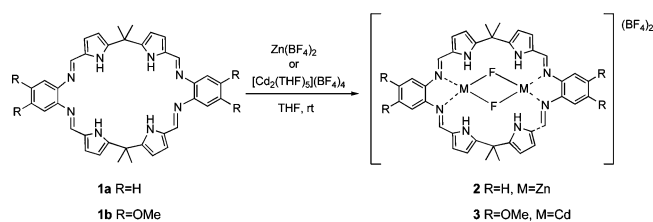
The dipyrromethane-based Schiff base type expanded porphyrin **1**, reported independently by our group and by Love and co-workers in 2003,⁶ has proven to be an efficient binucleating ligand. Only 4 years since its first reported synthesis, it is now appreciated that this macrocycle can

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Scheme 1



support a rich and diverse coordination chemistry.⁷ The molecular topology displayed by the complexes of macrocycle **1**, in which the two metal ions are held at relatively short distances (3.0–5.0 Å), provides an incentive for the study of transformations that require the cooperative action of the two Lewis acidic centers. These considerations, as well as current interest in developing fluoride abstraction chemistry (vide supra), prompted us to study the reactions of **1** with BF₄[−] salts of divalent metals. As described below, these efforts led to the successful isolation of fluoro-bridged complexes in the cases of Zn^{II} and Cd^{II}.

Treatment of the free base form of macrocycle **1** with Zn(BF₄)₂·5H₂O or [Cd₂(THF)₅](BF₄)₄ at room temperature resulted in the formation of the new complexes **2** and **3**, respectively (see Scheme 1). These compounds were characterized by X-ray diffraction analysis, NMR spectroscopy, and mass spectrometry (see the Supporting Information for full experimental details).

The crystal structure of the binuclear zinc complex **2** is shown in Figure 1. As previously observed for other bimetallic complexes of ligand **1a**,^{7c,d,f} the zinc centers are bound to the iminic nitrogens of the macrocycle but do not coordinate to the pyrrolic nitrogen atoms. Additionally, each zinc center is bound to a tetrafluoroborate anion and to two bridging fluoride ligands. The primary coordination sphere of both metal centers is completed by a bridging oxygen atom derived from an acetone molecule that resides within the wedgelike structure of the complex. As such, each zinc ion lies in a distorted octahedral geometry.

In spite of the numerous examples of fluoride ions bridging zinc cations in extended networks, very few discrete fluoro-bridged complexes have been structurally characterized. In complex **2**, the Zn–F_{bridge} distances (1.938–2.187 Å) fall within the range observed for other fluoride-bridged zinc complexes^{5,8,9} and are longer than those for zinc cations

coordinated to terminal fluoride ligands (ca. 1.85 Å).^{10,11} The rather long Zn–O distance of 2.254 Å is consistent with the acetone molecule being loosely bound to the metal centers. Interestingly, all of the pyrrolic NH protons of the macrocycle are engaged in hydrogen-bonding interactions with the bridging fluoride anions.

The ¹H NMR spectrum of **2** displays signals typical of those seen for other previously reported diamagnetic complexes of **1a**,^{7b–h} however, all of the observed resonances for **2** were characterized by significant peak broadening, possibly indicating a slow exchange between two or more conformational states in solution. No signals attributable to the fluoride ligands were observed in the ¹⁹F NMR spectrum of **2**. The absence of observable ¹⁹F NMR resonances for bridging fluorine ligands is a rather common phenomenon, and although its origin is not fully understood,^{1a} it has been attributed by others to interactions with the residual water in the deuterated solvents employed for the analyses.¹²

Interestingly, while this work was in progress, Love and co-workers reported an independent study involving the insertion of Zn into macrocycle **1a**.^{7d} These workers reported the preparation of a different Zn^{II}₂ complex of **1a** using Zn(BF₄)₂ as a zinc source. Although this species was not structurally characterized, combustion analysis of the isolated product was found to be compatible with the presence of four tetrafluoroborate anions and no fluoride bridges. To the extent that this latter structural assignment is correct, it would serve to highlight important, condition-based differences in the reactivity of **1a** with Zn(BF₄)₂ that would necessarily require further experimental study to elucidate fully.

The X-ray crystal structure of the cadmium complex **3** is depicted in Figure 2. The two cadmium cations are complexed within a distorted octahedral geometry, with each metal center being coordinated to two imine donors provided by the macrocycle, two bridging fluoride ligands, and two oxygen atoms from the water molecules.

The bridging Cd–F distances (2.221–2.246 Å) in complex **3** are relatively short as compared to the typical Cd–F bond lengths (typically in the 2.26–2.29 Å range) seen in extended networks containing Cd^{II} centers bridged by fluoride ions.¹³ Examples of well-characterized discrete fluoride-bridged cadmium complexes are extremely rare; however, the Cd–F distances in **3** are comparable to the ones reported in the case of one such system.⁵

As previously observed for complex **2**, each fluoride ligand in **3** is engaged in two hydrogen-bonding interactions with the pyrrolic NH protons of the macrocyclic ligand. Indeed, because of the highly ionic character of metal–fluorine bonds and the weak polarizability of the fluoride ion, metal-

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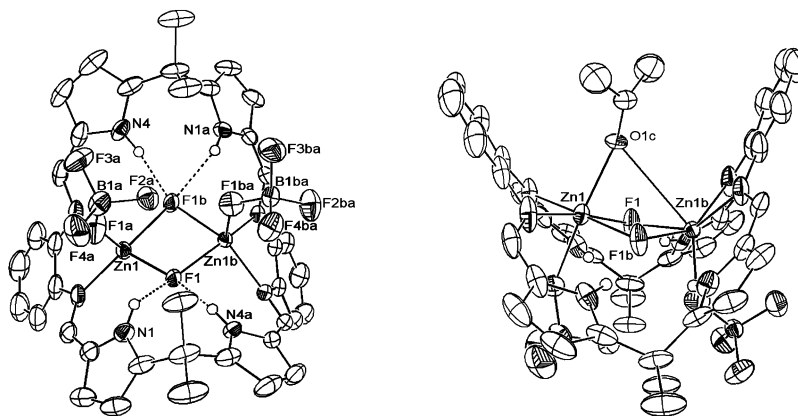


Figure 1. Top and side views of complex **2** showing a partial atom-labeling scheme. In the top view (left), the coordinated acetone molecule has been removed for clarity. Displacement ellipsoids are scaled to the 50% probability level. The macrocycle lies on a crystallographic twofold rotation axis at $1/2, y, 3/4$. The dashed lines are indicative of hydrogen-bonding interactions. Only one of the disordered ZnBF_4 ion pairs is shown; compare the Supporting Information for details.

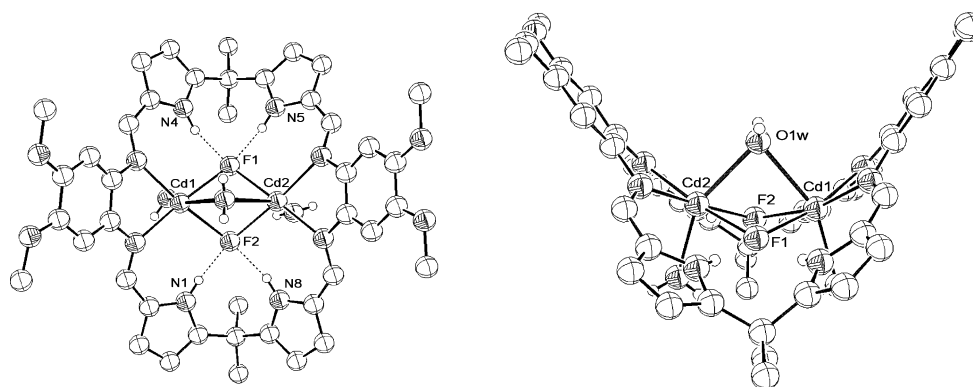


Figure 2. Top and side views of complex **3** showing a partial atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The dashed lines are indicative of hydrogen-bonding interactions.

coordinated fluoride ligands are often stabilized by additional interactions with Lewis acidic groups, such as hydrogen-bonding donors.³ As such, the availability of NH donors within the macrocyclic cavity that can support such noncovalent interactions likely serves to aid in the formation and stabilization of the fluoro-bridged complexes **2** and **3**.

In analogy to what was seen in the case of the zinc complex described above, the ^{19}F NMR spectrum of **3** shows only a single resonance corresponding to the tetrafluoroborate anion, with no signals attributable to the fluoride bridges being observed.

The Lewis acid promoted decomposition of the tetrafluoroborate anion can occur via two different mechanisms, namely, *fluoride abstraction* and *hydrolysis*. The mechanism of the formation of the fluoro bridges in complexes **2** and **3** was investigated through ^{19}F NMR spectroscopic analysis. In both cases, the ^{19}F NMR spectrum of the crude reaction mixture showed the expected resonance for the free tetrafluoroborate anion (at -154.5 ppm) and revealed the presence of BF_3 (at -148.6 ppm) as a reaction byproduct. These findings, as well as the lack of signals attributable to tetrafluoroborate hydrolysis products, are inconsistent with a hydrolysis-based mechanism. Accordingly, we attribute the

formation of the fluorine bridges seen in **2** and **3** to fluoride abstraction.

In summary, we have demonstrated that macrocycle **1** can be used to promote the abstraction of fluoride from tetrafluoroborate and concomitant formation of binuclear fluoro-bridged metal complexes in the case of Zn^{II} and Cd^{II} . This reactivity is unprecedented in the field of expanded porphyrin chemistry and fulfills a long-standing promise within the latter field, namely, the production of complexes wherein the cooperative action of two metal centers on a given substrate can be demonstrated. Efforts to generalize these findings to other metal systems and other expanded porphyrin-type ligands are currently in progress.

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Supporting Information Available: Synthetic details and X-ray structural data for complexes **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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