

Article

Fluoride Ion as Ligand and Hydrogen Bond Acceptor: Crystal Structures of Two Dinuclear Cu^{II} Complexes Built on a Diazecine Template

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Abstract: Two dinuclear Cu^{II} complexes based on a diazecine ligand were characterized by X-ray diffraction, one of which includes the rare Cu^{II}-F bond, resulting from dissociation of a BF₄⁻ ion. The F⁻ ligands actively participate in the crystal structure, behaving as acceptors for hydrogen bonding.

Keywords: copper; diazecine; hydrogen bond

1. Introduction

Relatively few coordination Cu^{II} complexes with coordinated fluoride ion [1] are described in the literature, compared to the solid-state materials bearing a Cu^{II}-F bond, which draw attention due to their particular magnetic properties [2,3]. Several qualitatively different approaches have been described for obtaining them. While the most direct method is the use of sparingly soluble CuF₂ as starting material [4–6], in most cases, the fluoride ion has come from an anion such as BF₄⁻ or PF₆⁻. The decomposition of BF₄⁻ to yield complexes, described by Reedijk *et al.* as early as 1974 [7], was later exploited in several groups for the preparation of a variety of coordination complexes with

terminal or bridged fluoride ligands, with different transition metal ions [8–14]. Several authors have described obtaining fluoro complexes “adventitiously” [15] or in purpose [16] when utilizing BF_4^- salts as metal sources, initially with Cu [9], and more recently with Cd [17], Zn [17], Cr [18] and Fe [19].

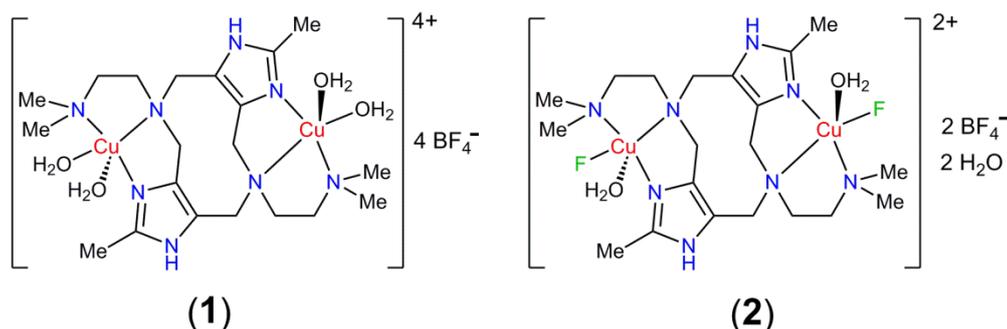
However, very little has been said about the factors promoting the incorporation of a F^- ligand from the dissociation of BF_4^- or PF_6^- anions, and apart from Reedijk’s early report [20] the corresponding mechanism remains virtually unexplored. Some authors claimed that bulky, very basic ligands [21], as well as the use of alcohols as solvent [16] promote dissociation of BF_4^- and PF_6^- . In several instances, complexes bearing a $\text{Cu}^{\text{II}}\text{--F}$ bond have resulted from exposure to oxygen of Cu^{I} complexes with BF_4^- [22] or PF_6^- [23–25] as counterions. It also seems that presence of sterically crowded and electron rich ligands, pointed out by Straub as essential for the formation of low-coordinate Cu^{I} species [23], could promote the dissociation of the fluoroanions and/or the stabilization of the coordinated fluoride.

In this context, we would like to contribute with the X-ray study of a couple of closely related dinuclear Cu^{II} complexes, in which a BF_4^- ion is the F^- source for the formation of $\text{Cu}^{\text{II}}\text{--F}$ bonds. The present study is of limited interest from a synthetic point of view, because of reproducibility and separation issues we were unable to address. However, this work clearly shows that X-ray diffraction allows the accurate assignment of F^- sites in the coordination sphere, and that this ligand is distinguishable from other potential ligands having almost similar scattering power, OH^- and H_2O , providing that each ligand affords a specific hydrogen bond pattern in the resulting crystal structure.

2. Results and Discussion

Both complexes are based on the octahydro[4,5]diimidazo[1,6]diazecine cyclic framework, abbreviated *dimeim* hereafter. This ligand has proven excellent for yielding di-copper complexes with a variety of counterions [26–28]. By reacting 2:1 equivalents of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and *dimeim* in methanol, we obtained the expected complex, $[\text{Cu}_2(\text{H}_2\text{O})_4(\textit{dimeim})](\text{BF}_4)_4$ (**1**, see Figure 1), a deep-blue compound initially intended for a study about the influence of the counterion on the magnetic properties of the cation. However, the very first crop of crystalline material contained light-blue small crystals, for which analytical data and X-ray crystallography gave a different formula, $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{F})_2(\textit{dimeim})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ (**2**, see Figure 1). The relative yields for **1** and **2** varied from synthesis attempts, and a satisfactory separation could not be achieved. However, on the basis of their colors, suitable single crystals for **1** and **2** were picked from the raw material, and their crystal structures determined.

Figure 1. Complexes **1** and **2** characterized by X-ray diffraction.

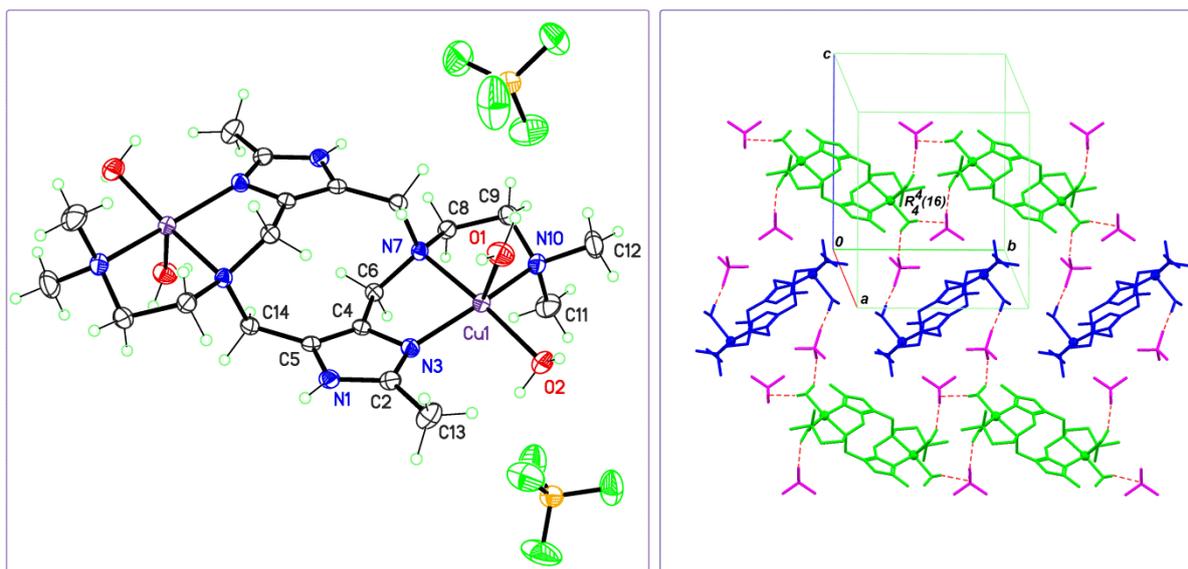


Numerous studies [26–30] carried out during the last ten years showed that the central 10-membered diazecine heterocycle of these compounds is systematically stabilized as a C_{2h} skewed boat-chair-boat conformer. Such a rigid, highly symmetrical conformation strongly favors the formation of centrosymmetric binuclear coordination compounds, using diazecine and imidazole N atoms as coordination sites [26–30]. This rule is again observed for **1** and **2**, two binuclear complexes with five-coordinate Cu^{II} centers.

2.1. $[Cu_2(H_2O)_4(dimeim)](BF_4)_4$ (**1**)

The major complex crystallizes with four BF_4^- anions and two independent half-cations in the asymmetric unit, each one completed to a full $[Cu_2(H_2O)_4(dimeim)]^{4+}$ cation through inversion centers (Figure 2). The same arrangement in a similar triclinic cell for the ClO_4^- salt of the same cation has been recently characterized [30], while a monoclinic polymorph of this compound, with an asymmetric unit containing a single $[Cu_2(H_2O)_4(dimeim)](ClO_4)_4$ formula, was previously reported [28]. These three closely related structures share a virtually identical conformation for the cation and present identical coordination geometries. In the crystal of **1**, a fit between independent cations gives a r.m.s. deviation which is less than 0.1 Å. The coordination sphere of the metal centers is closer to a square pyramidal (SP) geometry ($\tau_{Cu1} = 0.16$, $\tau_{Cu2} = 0.05$) with the apical positions occupied by water molecules. As expected, the angle restrictions induced by the chelate rings in the basal coordination planes (e.g., N3, N7, N10, O2 for Cu1; see Figure 2) push the metal from the base, by 0.246 Å (Cu1) or 0.212 Å (Cu2). In the crystal, cations and BF_4^- ions are held together by $OH\cdots F$ hydrogen bonds involving coordinated water molecules as donor groups (Table 1 and Figure 2). The resulting supramolecular structure is dominated by the formation of a $R_4^4(16)$ ring motif [31], which, interestingly, was also present in both polymorphs of the ClO_4^- salt [28,30].

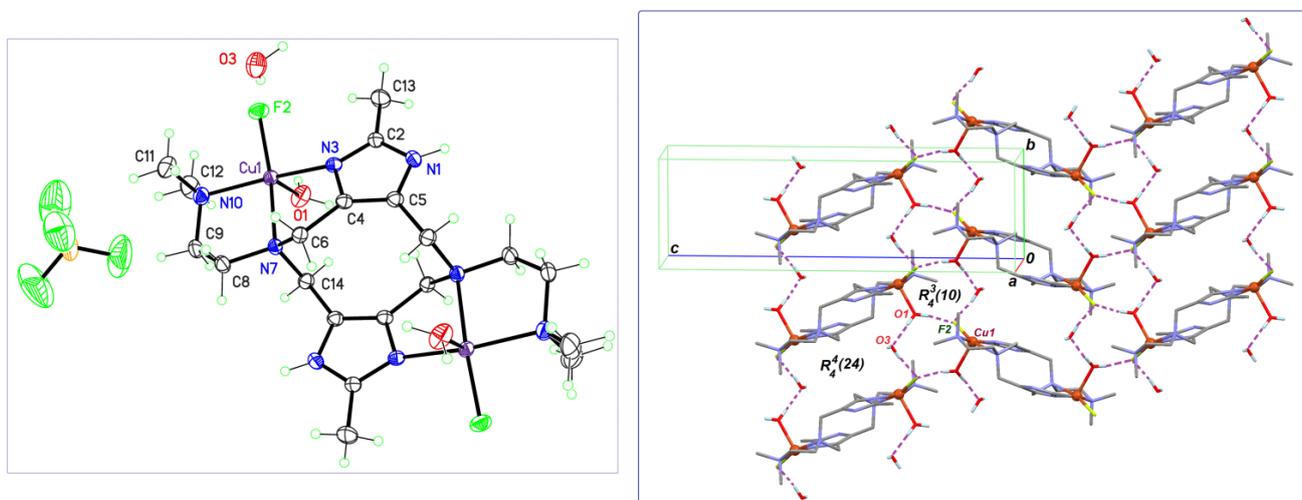
Figure 2. Left: ORTEP-like view of one cation and two anions in complex **1**; Right: Part of the crystal structure of **1**. Green and blue cations are based on Cu1 and Cu2, respectively. Dashed bonds represent the strongest hydrogen bonds formed between the coordinated water molecules and the BF_4^- ions (see Table 1).



2.2. $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{F})_2(\text{dimeim})](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}$ (**2**)

Complex **2** derives directly from **1**, by substitution of two coordinated water molecules in the basal planes by two F^- ions, affording cation $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{F})_2(\text{dimeim})]^{2+}$. Substituted water molecules are still present in the crystal, but now as lattice water molecules. Because of the charge drop for the cationic species, the formula is completed by two BF_4^- anions. The propensity of the diazecine cycle to be centrosymmetric is reflected in the composition of the asymmetric unit of **2**, limited to a half chemical formula (Figure 3).

Figure 3. Left: One cation, one anion, and one lattice water molecule in the crystal of **2**. Right: Part of the crystal structure of **2**, showing the main *R* ring motifs. BF_4^- anions as well as C- and N-bonded H atoms have been omitted for clarity. Dashed lines represent $\text{O1-H11}\cdots\text{F2}$, $\text{O1-H12}\cdots\text{O3}$, and $\text{O3-H32}\cdots\text{F2}$ hydrogen bonds (see Table 1).



Despite the substitution, the coordination of the metal center remains almost unchanged compared to **1**, with a square pyramidal geometry characterized by $\tau_{\text{Cu}} = 0.03$ and a deviation of Cu from the basal plane of 0.30 Å. The Cu–F bond length, 1.912(2) Å, is difficult to support, because few X-ray structures of Cu^{II} coordination complexes including such a bond have been reported so far. This bond length is however consistent with those found in available SP complexes with a basal Cu–F bond, 1.888 Å [15], 1.916 Å [16], and 1.902–1.932 Å [32]. Moreover, the definite proof of the presence of a Cu–F bond should be sought rather in the bond trans to the Cu–F bond. The Cu–N7 distance, 2.111(3) Å, is slightly larger than the expected distance, 2.053 Å, as spotted by MOGUL [33] on the basis of 15 hits. The corresponding bond length in the non-fluorinated complex **1**, is, for instance, $\text{Cu1-N7} = 2.088(4)$ Å and $\text{Cu2-N27} = 2.073(4)$ Å. The lengthening of the Cu–N7 bond in complex **2** should thus be regarded as a consequence of the difference in trans influence of the F^- ligand compared to H_2O .

As in **1**, the crystal structure in **2** is dominated by hydrogen bonds involving water molecules and F^- ions, although, in contrast to **1**, the most efficient acceptor in **2** is the F^- ligand coordinated to the metal center, F2 (see Table 1). Corresponding hydrogen bonds use the coordinated water molecule (O1) as well as the lattice water molecule (O3) as donor groups, and may be considered as strong interactions, with non bonding $\text{H}\cdots\text{F}$ distances of *ca.* 1.80 Å, and $\text{O-H}\cdots\text{F}$ angles close to 180° . It is worth noting

that the upper limit for very strong H \cdots F interactions in coordination chemistry is around OH \cdots F = 1.74(3) Å [15]. Based on these contacts, a 2D supramolecular structure is formed for compound **2**. First, $R_4^3(10)$ ring motifs are formed between cations and free water molecules, and edge-sharing motifs propagate in the [010] direction. The second base vector for the building of the 2D network is [001], and involves the same constituents to form $R_4^4(24)$ large rings (Figure 3). The lattice water molecule O3 is common to both R motifs, and should thus be seen as an essential component in the stabilization of the observed crystal structure.

Table 1. Main hydrogen bonds in complexes **1** and **2** involving water molecules as donor groups and F $^-$ or lattice water as acceptor groups. Weak N–H \cdots F contacts present in the crystal structures are not displayed in the table and may be found in the CIF deposited as supplementary material.

| O–H | Acceptor (F or O) | O–H (Å) | H \cdots A (Å) | O \cdots A (Å) | O–H \cdots A angle (°) | Symmetry for A |
|---|-------------------|-----------|------------------|------------------|--------------------------|-------------------------|
| [Cu₂(H₂O)₄(dimeim)](BF₄)₄ (1) | | | | | | |
| O1–H1B | F6 | 0.848(10) | 2.23(4) | 2.979(9) | 147(7) | x, y, z |
| O1–H1C | F14 | 0.848(10) | 2.030(15) | 2.870(7) | 171(6) | x, y, z |
| O2–H2B | F10 | 0.846(10) | 1.96(5) | 2.643(6) | 137(7) | x, y, z |
| O2–H2C | F5 | 0.845(10) | 2.11(4) | 2.858(8) | 148(7) | $1 - x, 1 - y, 1 - z$ |
| O21–H21B | F2 | 0.847(10) | 2.29(3) | 3.109(10) | 162(8) | $2 - x, 2 - y, -z$ |
| O21–H21C | F9 | 0.848(10) | 2.08(2) | 2.908(8) | 164(7) | $2 - x, 1 - y, -z$ |
| O22–H22B | F15 | 0.848(10) | 2.08(4) | 2.857(6) | 152(7) | $2 - x, 1 - y, 1 - z$ |
| O22–H22C | F3 | 0.849(10) | 1.782(18) | 2.624(9) | 172(7) | x, y, z |
| [Cu₂(H₂O)₂(F)₂(dimeim)](BF₄)₂·2H₂O (2) | | | | | | |
| O1–H11 | F2 | 0.848(10) | 1.798(15) | 2.635(3) | 169(5) | $-x, y - 1/2, -z + 1/2$ |
| O1–H12 | O3 | 0.846(10) | 1.873(12) | 2.716(4) | 174(5) | $x, y - 1, z$ |
| O3–H31 | F14 | 0.845(10) | 1.911(19) | 2.736(6) | 165(6) | $x - 1, y - 1, z$ |
| O3–H32 | F2 | 0.847(10) | 1.804(13) | 2.644(4) | 171(5) | x, y, z |

3. Experimental Section

Synthesis of the complexes. The ligand *dimeim* was prepared as previously described [26]. To 50 mL of a methanolic solution containing two mmol of Cu(BF₄)₂·6H₂O, one mmol of solid *dimeim* was added in several portions, which dissolved upon coordination. Small light blue crystals of **2** were collected after one day, calculated analysis for [Cu₂(H₂O)₂(F)₂(*dimeim*)](BF₄)₂·2H₂O: C, 30.05; H, 5.55; N, 14.02%. Found: C, 30.46; H, 5.85; N, 14.27%. Deep blue crystals of **1** were collected after a few days. Calculated analysis for [Cu₂(H₂O)₄(*dimeim*)](BF₄)₄: C, 25.69; H, 4.74; N, 11.99%. Found: C, 25.38; H, 4.74; N, 11.93%.

X-ray diffraction. Data for complexes **1** and **2** were collected at room temperature on a Bruker P4 diffractometer [34] using the Mo-K α radiation (Table 2). Raw data were corrected for absorption effects [35] and the structures refined with the SHELX programs [36]. Although sample for **2** was a rather long crystal not uniformly irradiated during data collection, a reduction of the sample size was not intended, because very few single crystals were available. However, we assume that absorption correction for **2** is still reliable ($R_{\text{int}} = 0.028$). Accurate determination of sites occupied by H atoms was critical for water molecules, in order to discriminate F $^-$ and water molecules (and possibly OH $^-$ groups,

assuming that hydroxyl groups could be present in the reaction media). All water H atoms in both complexes were thus assigned from difference maps, and refined with free coordinates, although soft restraints were applied to O–H bond lengths and H···H separations, 0.85(1) and 1.34(1) Å, respectively. Sensible orientations for water molecules are obtained in the final models, since all O–H groups are engaged in efficient hydrogen bonds. On the other hand, in the case of **2**, final difference map is featureless in the vicinity of the coordinated fluoride site, corroborating that Cu–F bonds have been formed, rather than Cu–OH or Cu–OH₂ bonds. CIF data, including structure factors, are deposited as supplementary material.

Table 2. Crystal data for complexes **1** and **2**.

| Compound | 1 | 2 |
|---|--|--|
| Empirical formula | C ₂₀ H ₄₄ B ₄ Cu ₂ F ₁₆ N ₈ O ₄ | C ₂₀ H ₄₄ B ₂ Cu ₂ F ₁₀ N ₈ O ₄ |
| Formula weight | 934.95 | 799.33 |
| Color, habit | blue prism | blue prism |
| Crystal size [mm] | 0.40 × 0.40 × 0.20 | 0.68 × 0.20 × 0.12 |
| Space group | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> [Å] | 9.455(2) | 10.4816(9) |
| <i>b</i> [Å] | 12.0445(17) | 7.0223(7) |
| <i>c</i> [Å] | 16.493(2) | 22.732(3) |
| α [°] | 87.469(10) | - |
| β [°] | 83.061(14) | 95.913(8) |
| γ [°] | 75.465(14) | - |
| <i>V</i> (Å ³) | 1804.7(5) | 1664.3(3) |
| <i>Z</i> | 2 | 2 |
| $\rho_{\text{calcd.}}$ [g·cm ⁻³] | 1.721 | 1.595 |
| μ [mm ⁻¹] | 1.303 | 1.374 |
| 2 θ range [°] | 4–52.5 | 4–50 |
| Reflections collected | 14469 | 5831 |
| Independent reflections (<i>R</i> _{int}) | 7246 (0.031) | 2924 (0.028) |
| Transmission factors [min., max.] | 0.310–0.356 | 0.244–0.296 |
| Final <i>R</i> indices [<i>I</i> ≥ 2 σ (<i>I</i>)] <i>R</i> ₁ , <i>wR</i> ₂ | 0.063, 0.173 | 0.042, 0.113 |
| Final <i>R</i> indices (all data) <i>R</i> ₁ , <i>wR</i> ₂ | 0.075, 0.181 | 0.058, 0.128 |
| Goodness-of-fit on <i>F</i> ² | 1.118 | 1.055 |
| Data/restraints/parameters | 7246/12/517 | 2924/6/224 |
| Largest difference peak/hole [e Å ⁻³] | 0.87, -0.52 | 0.75, -0.78 |

4. Conclusions

In conclusion, substitution of basal water by F⁻ ligand in complex **1**, and concomitant release of water to form the hydrate **2**, allows the stabilization of a crystal structure featuring strong intermolecular hydrogen bonds between coordinated and free water molecules and the fluoride ligands, which also act as acceptors for hydrogen bonding.

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References and Notes

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