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Fluoro Metallacrown Compounds

A Hexacopper Fluoro Metallacrown Cavitand and its Alkali-Metal Complexes**

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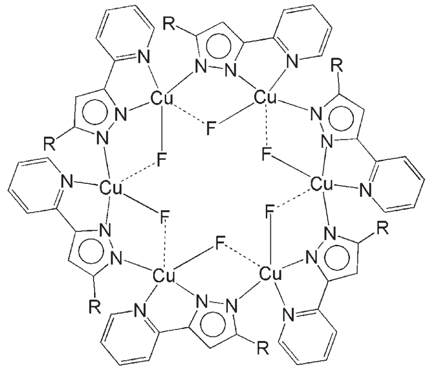
Metallacrowns are cyclic metal–organic compounds bearing donor atoms oriented towards their central cavity.[1,2] They resemble crown ethers in their ability to bind an additional metal ion at their center, and a nomenclature based on that used for crown ethers has been adopted for them.[1] Many metallacrowns are constructed using polydentate hydroxamate-containing ligands,[1] although examples derived from hydrazido,[3,4] pyridonate[2,5] and poly(ethanol)amine[6] derivatives are also known. The central donor atoms in these compounds are part of the organic ligand, and metallacrown (MC) ring sizes ranging from [9]MC-3[1] to [36]MC-12[7] have been reported, either in the presence or absence of a central metal ion. A related class of compound are molecular wheels, which generally contain smaller bridging ligands such as alkoxides,[8] hydroxide,[9,10] and/or fluoride.[11,12] The central cavities in crystalline molecular wheels are often empty, although there are examples with bound anionic[10] or inorganic[13] or organic[12] cationic guests. As a continuation of our work in pyrazole inorganic supramolecular chemistry,[14–16] we report three complexes derived from 3{5}-(pyrid-2-yl)-5{3}-(*tert*-butyl)pyrazole (HL) and $\mathrm{CuF_2}$. The common motif in these compounds is $[\{\mathrm{Cu}(\mu\text{-F})(\mu\text{-L})\}_6]$ (**1**, Scheme 1), a molecular wheel that complexes alkali metals through its $\mathrm{F^-}$ centers. Hence, **1** can be considered as the first metal fluoro metallacrown and as a rare example of a metallacrown isolated both in the presence and the absence of a central complexed metal ion.[2]

Treatment of $\mathrm{CuF_2}$ with 1 equivalent of HL[17] and $n\mathrm{Bu_4NOH}$ in MeOH at room temperature yields a green solution. Evaporation of the solution to dryness and recrystallization of the solid residue from $\mathrm{CH_2Cl_2}$/pentane affords turquoise crystals, formulated as $[\{\mathrm{Cu}(\mu\text{-F})(\mu\text{-L})\}_6(\mathrm{H_2O})_2]\cdot 8\,\mathrm{CH_2Cl_2}$ ($[\mathbf{1}(\mathrm{H_2O})_2]\cdot 8\,\mathrm{CH_2Cl_2}$) from the crystallographic analysis described below. Analogous reactions using NaOH or KOH as base proceeded similarly, affording $[\mathrm{Na}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{HF_2}\cdot 3.2\,\mathrm{CH_2Cl_2}\cdot 0.66\,\mathrm{O(C_2H_5)_2}$ and $[\mathrm{K}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{F_{0.6}(HF_2)_{0.4}}\cdot 3.5\,\mathrm{CH_2Cl_2}$.[18] The different anion content given for these non-isostructural compounds is based on their crystallographic formulations, but is also consistent with their microanalyses (see the Supporting Information). The compounds lose their crystallinity in vacuo. The resultant powders give microanalyses consistent with their formulation as $[\mathbf{1}(\mathrm{H_2O})_2]\cdot 3\,\mathrm{CH_2Cl_2}$, $[\mathrm{Na}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{HF_2}\cdot\mathrm{CH_2Cl_2}$, and $[\mathrm{K}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{F_{0.6}(HF_2)_{0.4}}$. The presence of water in dried $[\mathbf{1}(\mathrm{H_2O})_2]\cdot 3\,\mathrm{CH_2Cl_2}$ was confirmed by its IR spectrum, in which a δ(H-O-H) vibration at 1650 cm^{-1} is observed.[19] This vibration is not shown by the other two compounds, while the ^{1}H NMR spectra of all three solids in $\mathrm{CD_3NO_2}$ contain peaks at $\delta = 6.5$ ppm, assignable to 2–3 equivalents of $\mathrm{CH_2Cl_2}$. Some preparations of $[\mathbf{1}(\mathrm{H_2O})_2]$ were contaminated by $[\mathrm{Na}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{HF_2}$, presumably by leaching of $\mathrm{Na^+}$ ions from the glass crystallization vials, and all measurements of $[\mathbf{1}(\mathrm{H_2O})_2]\cdot 3\,\mathrm{CH_2Cl_2}$ were performed using a sample that was sodium-free as judged by microanalysis.



Scheme 1. Structure of the metallacrown **1** (R = *tert*-butyl). The dashed lines show the longer apical Cu–F bonds at the square-pyramidal Cu^{2+} centers.

The single-crystal X-ray structure of $[\mathbf{1}(\mathrm{H_2O})_2]\cdot 8\,\mathrm{CH_2Cl_2}$ contains a centrosymmetric cyclic hexanuclear complex with only small deviations from idealized S_6 symmetry (Figure 1, Table 1). Each of the three unique Cu^{2+} ions has a square-pyramidal coordination geometry ($\tau = 0.004(3)$–$0.060(3)$[20]), with one chelating L$^-$ ligand that forms a 1,2-bridge to a neighboring Cu^{2+} ion through its pyrazolido group. The metal ions are also linked by μ-F$^-$ ligands, which bridge between a basal coordination site of one Cu^{2+} ion and the apical site of the other. All Cu–N and Cu–F bond lengths in the molecule have typical values, and Cu···Cu distances range from

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Supporting information (experimental and crystallographic details, as well as a figure emphasizing the double-cone shape of **1** and figures of the magnetic and EPR data) for this article is available on the WWW under http://www.angewandte.org or from the author.

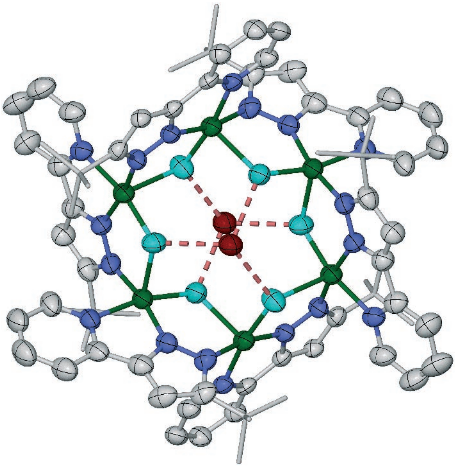

Figure 1. View of the $[\{Cu(\mu\text{-}F)(\mu\text{-}L)\}_6(H_2O)_2]$ molecule in the crystal structure of $[\mathbf{1}(H_2O)_2]\cdot 8\,CH_2Cl_2$. Thermal ellipsoids are set at 50% probability for all atoms except those of the *tert*-butyl groups, which have been deemphasized; all H atoms and alternative disorder sites have been removed for clarity. C gray, Cu green, F cyan, N blue, O red.

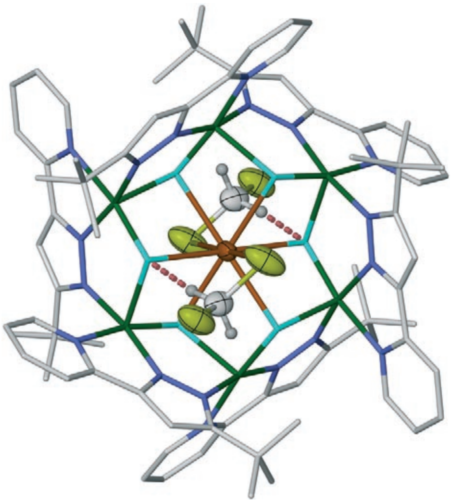

Figure 2. View of the $[K\{Cu(\mu_3\text{-}F)(\mu\text{-}L)\}_6(CH_2Cl_2)_2]^+$ ion in the crystal structure of $[K\subset\mathbf{1}(CH_2Cl_2)_2]F_{0.6}(HF_2)_{0.4}\cdot 3.5\,CH_2Cl_2$. For clarity, all atoms from the metallacrown have been deemphasized, and all H atoms and minor disorder sites have been removed from this moiety; thermal ellipsoids for the other atoms are set at 50% probability. C light gray, H dark gray, Cl light green, Cu green, F cyan, K orange, N blue.

3.4948(7)–3.5112(7) Å. The L^- ligands project out of the plane of the $\{Cu_6F_6\}^{6+}$ ring, forming a double-bowl shape above and below the molecule. The base of each bowl is formed by three of the six F atoms and has a diameter of 2.1 Å measured from their van der Waals surfaces. The diameter at the rim of the cavity is approximately 5.6 Å (defined by the three inward-facing methyl substituents) and its height is 6.5 Å, although these measurements are complicated by *tert*-butyl group disorder. Each cavity in **1** contains a disordered water molecule, which lies within hydrogen-bonding distance of two (minor disorder site) or all three (major site) F atoms on the inner face of the bowl (O···F 2.478(4)–2.734(15) Å, Figure 1).

Table 1: Selected metric parameters for the crystal structures of **1** and its alkali-metal complexes.

	$[\mathbf{1}(H_2O)_2]$	$[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$	$[K\subset\mathbf{1}(CH_2Cl_2)_2]F_{0.6}(HF_2)_{0.4}$
Cu−N [Å]	1.914(3)–2.060(3)	1.931(3)–2.075(3)	1.940(4)–2.062(4)
Cu−F, basal [Å]	1.934(2)–1.945(2)	1.905(2)–1.922(2)	1.896(2)–1.914(2)
Cu−F, apical [Å]	2.237(2)–2.280(2)	2.193(2)–2.244(2)	2.210(2)–2.273(2)
Cu-F-Cu [°]	112.10(10)–113.24(11)	111.67(9)–113.13(9)	113.38(11)–115.91(11)
Cu···Cu [Å]	3.4948(7)–3.5112(7)	3.4232(6)–3.4611(6)	3.4851(8)–3.5191(8)
τ[a]	0.004(3)–0.060(3)	0.014(3)–0.079(3)	0.016(3)–0.060(3)
M−F [Å][b]	–	2.420(2)–2.486(2)	2.601(3)–2.630(2)
M−Cl [Å][b]	–	3.7243(15)	3.7082(17)
Cu···M [Å][b]	–	3.4232(4)–3.4494(4)	3.4941(6)–3.5027(5)
Cavity: base diameter × rim diameter × height [Å]	2.1(1) × 5.6(6) × 6.5(2)	1.9(1) × 5.0(4) × 6.8(2)	2.2(1) × 4.7(2) × 6.4(1)

[a] See ref. [20] for the definition of τ. [b] M = Na or K.

The metallacrown rings in $[M\subset\mathbf{1}(CH_2Cl_2)_2]^+$ (M = Na, K) have the same connectivity as metal-free $[\mathbf{1}(H_2O)_2]$ (Figures 2 and 3). The alkali-metal cations lie on crystallographic inversion centers, being complexed by the six F donors of the metallacrown and by two axial M···Cl interactions of 3.7 Å to the CH_2Cl_2 molecules lying within the bowl-shaped cavities of the crown. The bond lengths and angles in the metallacrown ligands show some small differences between the three compounds (Table 1), but there is no obvious trend relating these small variations to the radii of the complexed alkali-metal ions. The base of the bowl-shaped cavity is 0.2–0.3 Å narrower in $[Na\subset\mathbf{1}(CH_2Cl_2)_2]^+$ compared to the other two structures, reflecting the short Na−F bond lengths in this compound (Table 1). Differences in the other dimensions of the cavities in $[\mathbf{1}(H_2O)_2]$ and $[M\subset\mathbf{1}(CH_2Cl_2)_2]^+$ are greater, but these mostly reflect differing *tert*-butyl group positions and disorder in the molecules. In addition to the M···Cl contact, each of the complexed CH_2Cl_2 molecules forms a hydrogen bond to an F atom of the host cavitand, with C···F 3.044(5)–3.064(6) Å (dashed red lines in Figure 2).

The variable-temperature magnetic behavior of the three dried solids is very similar. For each material, $\chi_M T = 2.2\ cm^3\,mol^{-1}\,K$ at 300 K, slightly below the value expected for six independent Cu^{2+} spins (ca. $2.5\ cm^3\,mol^{-1}\,K$). The value of $\chi_M T$ decreases upon cooling, becoming essentially zero below 15 K (Figure 4). The data were modeled by the van Vleck equation from matrix diagonalization of a six-fold symmetric Hamiltonian [Eq. (1), S_1–$S_6 = \frac{1}{2}$]. This analysis

$$H = -2J(S_1 S_2 + S_2 S_3 + S_3 S_4 + S_4 S_5 + S_5 S_6 + S_6 S_1) \qquad (1)$$

gives $g = 2.11(1)$–$2.12(1)$ and $-15.0(1) \leq J \leq -13.5(1)\ cm^{-1}$ for the three compounds (Figure 4). These J values are typical for Cu^{2+} ions linked by one bridging pyrazolido

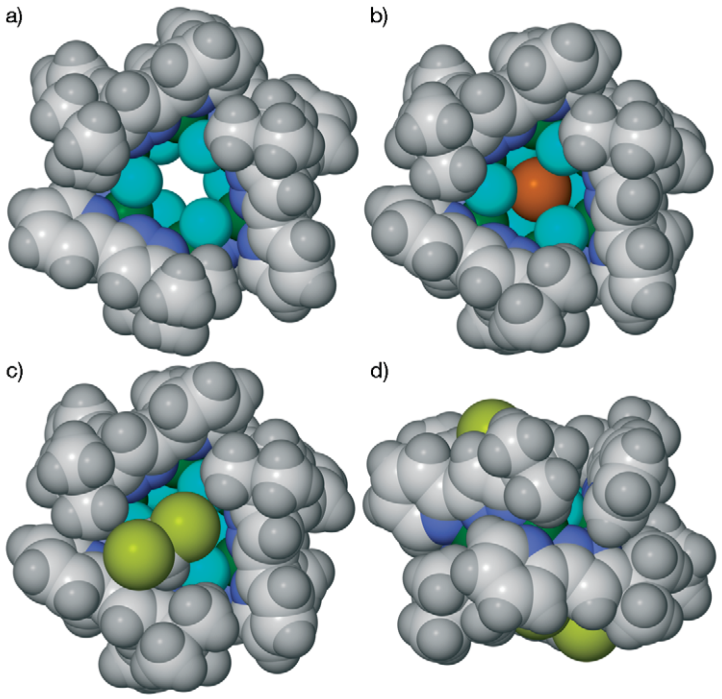

Figure 3. Space-filling models: top views of a) the molecule **1** in $[\mathbf{1}(H_2O)_2]$, b) the $[K\subset\mathbf{1}]^+$ cation, and c) the $[K\subset\mathbf{1}(CH_2Cl_2)_2]^+$ cation, showing one of the included CH_2Cl_2 molecules; d) side-on view of the $[K\subset\mathbf{1}(CH_2Cl_2)_2]^+$ cation. C light gray, H dark gray, Cl light green, Cu green, F cyan, K orange, N blue.

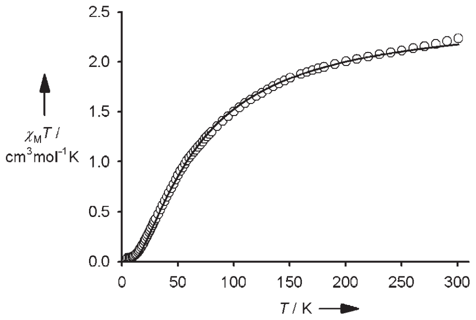

Figure 4. Variable-temperature magnetic data for powdered $[\mathbf{1}(H_2O)_2]\cdot 3\,CH_2Cl_2$ (○) and their best fit to the van Vleck equation derived from Equation (1) (——). The equivalent data from $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot CH_2Cl_2$ and $[K\subset\mathbf{1}(CH_2Cl_2)_2]F_{0.6}(HF_2)_{0.4}$ are almost superimposable on those shown here.

ligand[21] (the basal/apical fluoro bridges should make a much smaller contribution to superexchange in **1**), while the g values are close to those derived by EPR spectroscopy (see below). Clearly, complexation of **1** by Na^+ or K^+ has little effect on its magnetic behavior. This result is reasonable, since the geometry of the principal covalent superexchange pathway in **1**, the pyrazolido bridging units, is essentially the same in all three compounds.

The X-band EPR spectra of solid $[\mathbf{1}(H_2O)_2]\cdot 3\,CH_2Cl_2$ and its complexes between 115–293 K are essentially identical. Each of them show an isotropic line at $g = 2.13$ and a weak half-field resonance near 1590 G. The compound $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot CH_2Cl_2$ was examined more thoroughly with a Q-band EPR spectrum, which also shows an isotropic signal at $g = 2.13$ that slowly resolves below 100 K into a rhombic pattern, with $g_1 = 2.20$, $g_2 = 2.12$, and $g_3 = 2.06$ at 30 K and a weak half-field signal as before. Further cooling leads to weakening of this signal, as the diamagnetic ground state of the compound is increasingly populated, without affording additional resolution.

In conclusion, **1** is a metallacrown with only a small degree of conformational flexibility and is pre-organized to bind Na^+ and K^+ ions. This conclusion is reinforced by the observation that attempted syntheses of $[Li\subset\mathbf{1}(CH_2Cl_2)_2]^+$ and $[Cs\subset\mathbf{1}(CH_2Cl_2)_2]^+$ using the appropriate alkali-metal hydroxides gave low yields of $[Na\subset\mathbf{1}(CH_2Cl_2)_2]^+$ as the only isolable product, which arises either from a sodium impurity in the bases used,[5] or by leaching from pyrex glassware (as above). All the compounds of **1** isolated in this study contain water or CH_2Cl_2 complexed in the cavities on either side of the crown. Compound **1** can therefore also be considered as a new bowl-shaped host, with a cavity about 50% deeper than that of the similarly-shaped receptor cyclotriveratrylene.[22] Studies of the affinity of **1** and its complexes towards other inorganic and organic guests are in progress.

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[18] CCDC-632655 ($[\mathrm{Na}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{HF_2}\cdot 3.2\,\mathrm{CH_2Cl_2}\cdot 0.66\,\mathrm{O(C_2H_5)_2}$), CCDC-632657 ($[\mathrm{K}\subset\mathbf{1}(\mathrm{CH_2Cl_2})_2]\mathrm{F_{0.6}(HF_2)_{0.4}}\cdot 3.5\,\mathrm{CH_2Cl_2}$), and CCDC-632657 ($[\mathbf{1}(\mathrm{H_2O})_2]\cdot 8\,\mathrm{CH_2Cl_2}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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