Inorg. Chem. **1992,** *31,* 4436–4438

A New Fluorinated Tetraalkoxide Ligand Derived from the Hydration of Hexafluoroacetylacetone

Elisabeth Bouwman, John C. Huffman, Emil B. Lobkovsky, and George Christou*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Hui-Lien Tsai and David N. Hendrickson*

Department of Chemistry-0506, University of California at San Diego, La Jolla, California 92093-0506

Received May 20, 1992

We wish to report the initial examples of the use of the tetraol derived from the hydration of hexafluoroacetylacetone as a ligand to metals, namely the transition metals manganese and iron. We also report that, in the particular bridging mode that it adopts in the described Mn^{III}_2 complex, it is capable of supporting *ferromagnetic* exchange interactions between metal centers. We believe this molecule has great potential as a generally-useful new polyfunctional ligand in metal chemistry and that it will thus prove attractive to a variety of inorganic chemists.

Hexafluoroacetone (**1**) has long been known[1] to add water to give the stable hydrate hexafluoro-2,2-propanediol (**2**), which, on deprotonation, can function as a dianionic ligand (**3**) to main group[2] and transition[3] metals (Figure 1). However, the hydration of hexafluoroacetylacetone (hfacH; **4**) to yield 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (hfptH_4; **5**), although known,[4] has not led to similar investigation of the ability of the deprotonated form (**6**) to form metal complexes. Instead, the nearest to this that has been reported is attack of OH^- on $hfac^-$ (**7**) to yield the deprotonated monohydrate (**8**);[5–7] however, in the product $[Co(en)_2(hfacOH)]Br{\cdot}H_2O$,[8] the OH group is noncoordinated and the ligand **8** is behaving like a dianionic version of **7**. The same behavior has been observed for $[Cr(en)_2(hfac)](PF_6)(ClO_4)$.[9] Similarly, attack by MeO^- on **7** gives the methoxide adduct $hfacOMe^{2-}$ (**9**) in $[Co(trien)(hfacOMe)](ClO_4)$.[10]

The tetraol **5** was originally obtained in low yield as a white crystalline solid during the preparation of hfacH (**4**).[4] It was mentioned that an ethereal solution of **4** shaken with a little water gives **5**, as evidenced by a negative test for the diketone. Using this observation, we have devised a convenient means of preparing high yields of **5** from commercially-available **4**. To a toluene solution (20 mL) of **4** (2.0 mL, 14 mmol) was added water (0.51 g, 28 mmol). The two-phase system was shaken occasionally and maintained at ambient temperature. Crystallization of a white solid began after ca. 15 min. When this was complete, the solid was collected by filtration, washed with toluene, and dried in air. The yield is 80–85%. The solid can be recrystallized from hot water. The material is analytically pure,[11] and its tetraol nature was confirmed by X-ray crystallography.[12]

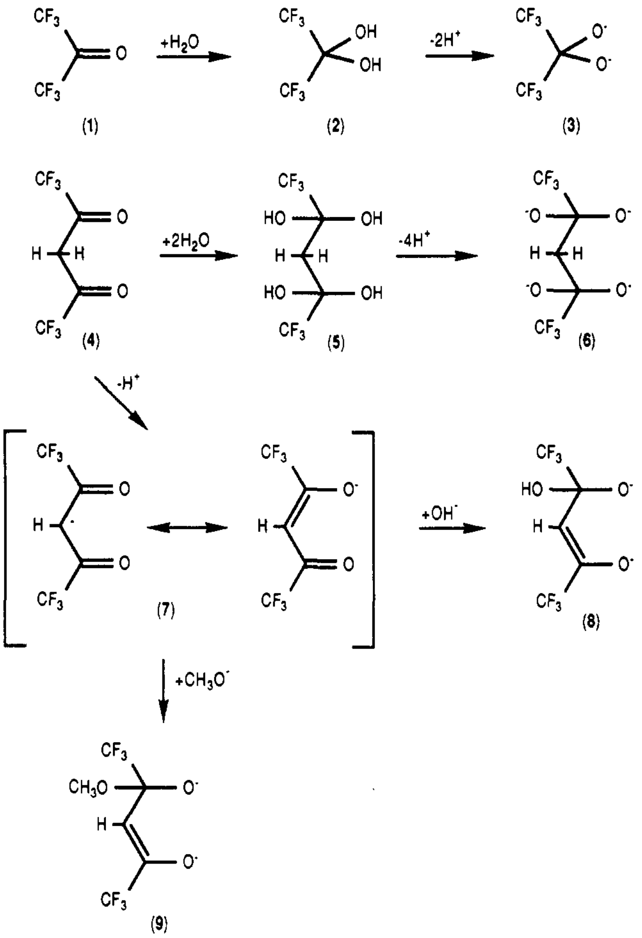

Figure 1. Depiction of the various forms of hexafluoroacetone (**1**) and hexafluoroacetylacetone (**4**) mentioned in the text.

A filtered solution of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ (0.50 mmol), a convenient source of Mn^{III}, and py (4.5 mmol) in CH_2Cl_2 (20 mL) was treated with **5** (0.75 mmol) in MeCN (0.5 mL) and **4** (3.0 mmol). The homogeneous reaction solution was stored in a freezer overnight, and the resulting dark brown microcrystalline precipitate of $(pyH)_2[Mn_2(hfac)_4(hfpt)]$ (**10**)[13] was collected by filtration; the yield was ~60%. An analogous reaction was performed by employing $[Fe_3O(OAc)_6(py)_3](ClO_4)$. After overnight storage of the reaction solution in a freezer, well-formed yellow-green crystals of $(pyH)[Fe(hfac)_2(hfptH_2)]$ (**11**) were collected by filtration; the yield was 19% (based on Fe).[14]

The structures of the anions of **10**[15,16] and **11**[15] are shown in Figure 2. The anion of **10** has crystallographically-imposed C_2 symmetry, the rotation axis passing through the central carbon atom of the $hfpt^{4-}$ ligand. The bridging tetradentate $hfpt^{4-}$ ligand occupies two sites at each octahedral Mn^{III} center, the other sites

---

(1) Middleton, W. J.; Lindsey, R. V. *J. Am. Chem. Soc.* **1964,** *86,* 4948.

(2) (a) Prager, J. H.; Ogden, P. H. *J. Org. Chem.* **1968,** *33,* 2100. (b) Ogden, P. H.; Nicholson, G. C. *Tetrahedron Lett.* **1968,** 3553.

(3) Bradford, P.; Hynes, R. C.; Payne, N. C.; Willis, C. J. *J. Am. Chem. Soc.* **1990,** *112,* 2647.

(4) Schultz, B. G.; Larsen, E. M. *J. Am. Chem. Soc.* **1949,** *71,* 3250.

(5) Kuroda, K. *Chem. Lett.* **1979,** 93.

(6) Aygen, S.; Kitamura, Y.; Kuroda, K.; Kume, R.; Kelm, H.; van Eldik, R. *Inorg. Chem.* **1985,** *24,* 423.

(7) Fukuda, Y.; Ishige, M.; Ito, T.; Kuroda, K.; Sone, K.; Susuki, Y.; Yano, S.; Yoshikawa, S. *Chem. Lett.* **1981,** 1699.

(8) Aygen, S.; Paulus, E. F.; Kitamura, Y.; van Eldik, R. *Inorg. Chem.* **1987,** *26,* 769.

(9) Katou, T.; Yamamoto, Y.; Kuroda, K.; Watanabe, K.; Kitamura, Y. *Inorg. Chim. Acta* **1981,** *180,* 13.

(10) Kitamura, Y.; Leipoldt, J. G.; Roodt, A. *Inorg. Chim. Acta* **1988,** *149,* 125.

(11) Anal. Calcd (found) for $C_5H_6F_6O_4$: C, 24.60 (24.69); H, 2.48 (2.51).

(12) Bouwman, E.; Huffman, J. C.; Caulton, K. G.; Christou, G. Unpublished results.

(13) Complex **10** was originally obtained in very small yield, in a form suitable for crystallography, from the reaction of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ with hfacH and py. The described procedure is the result of yield optimization after the identity of **10** was determined by crystallography.

(14) Attempts to increase the yield by varying reaction conditions and ratios were plagued by contamination of product with $Fe_2(OH)_2(hfac)_4$.

0020-1669/92/1331-4436$03.00/0 © 1992 American Chemical Society

being occupied by hfac ligands in their familiar bidentate chelating modes. The Mn^{III} atoms are six-coordinate and demonstrate the Jahn–Teller distortion expected for a high-spin d^4 metal; axial elongation is clearly evident with Mn1–O20 and Mn1–O22 distances (2.219 (8) and 2.228 (8) Å, respectively) significantly longer than the rest (1.859 (8)–2.017 (7) Å). The $hfpt^{4-}$ ligand bridges such that one alkoxide oxygen from each *gem*-diol pair is attached to a particular Mn^{III} atom; thus, two six-membered chelate rings are formed, and the alkoxide oxygens are all *terminally* coordinated. The latter results in Mn1–O17 and Mn1–O18 (1.875 (7) and 1.859 (8) Å, respectively) being shorter than Mn1–O19 and Mn1–O21 (2.017 (7) and 1.972 (7) Å, respectively), as expected for terminal Mn–alkoxide vs Mn–diketonate bonds. The two Mn^{III} equatorial planes form a dihedral angle of 137.7°. The saturated nature of the bridging ligand is supported by C–C (1.522 (14) and 1.547 (16) Å) and C–O (1.372 (13) and 1.393 (13) Å) distances that are consistent with single bonds (1.54 and 1.43 Å, respectively). The pyH^+ cations are associated with the anion in the solid state; they are hydrogen-bonded to O17 and O17′ with N–H··O distances of 2.74 Å.

In contrast to **10**, the anion of **11** is mononuclear in Fe^{III}. As shown in Figure 2, one of each *gem*-diol pair of oxygen atoms (O41 and O42) remains protonated and unbound to the metal. The resulting $hfptH_2^{2-}$ ligand is thus in a bidentate chelating mode to Fe^{III}, in a fashion similar to that of each Mn^{III} in **10**. The unbound –OH groups are hydrogen-bonded to the –OH groups of a neighboring molecule, yielding a weakly linked dimeric unit in the solid state that comprises the contents of the asymmetric unit; the two independent mononuclear units are extremely similar in structure. The Fe^{III}–O bond lengths are in the range 1.905 (4)–2.096 (5) Å, with the Fe^{III}–O(alkoxide) distances (1.905 (4)–1.936 (5) Å) being noticeably shorter than Fe^{III}–O(diketonate) distances (2.032 (4)–2.096 (5) Å).

Variable-temperature solid-state magnetic susceptibility studies have been performed on powdered samples of complex **10** (restrained in parafilm to prevent torquing) in the temperature range 5.01–320 K in order to characterize the sign and magnitude of the magnetic exchange interaction propagated by this unusual bridging ligand. The effective magnetic moment, μ_{eff}, per Mn_2 molecule slightly rises from 6.73 μ_B at 320 K to a maximum of 6.75 μ_B at 70.0 K, whereupon there is a gradual decrease to 6.67 μ_B at 20 K, followed by a more rapid decrease to 5.96 μ_B at 5.01 K. A full-matrix diagonalization approach, including magnetic exchange ($-2J\hat{S}_1\cdot\hat{S}_2$), axial single-ion zero-field ($D\hat{S}_z^2$), and isotropic Zeeman interactions, was employed to fit the data. A local minimum in the least-squares error function with $J < 0$ could be found; however, the global minimum was found with $J = +0.35$ cm^{-1}, $D = 0.9$ cm^{-1}, and $g = 1.94$. This was checked by collecting data both at 10.0 and 50.0 kG in the 2.00–30.0 K range. These two data sets were fit together to give $J = +0.21$ cm^{-1}, $D = 0.9$ cm^{-1}, and $g = 1.99$. Thus, we conclude there is a very weak ferromagnetic interaction. The latter result is not particularly surprising, since the saturated nature of the $hfpt^{4-}$ ligand's carbon backbone and the particular bridging mode that it adopts in **10** enforces orthogonality of the Mn^{III} magnetic orbitals. Also, the long Mn··Mn distance (4.641 (5) Å) precludes direct through-space overlap.

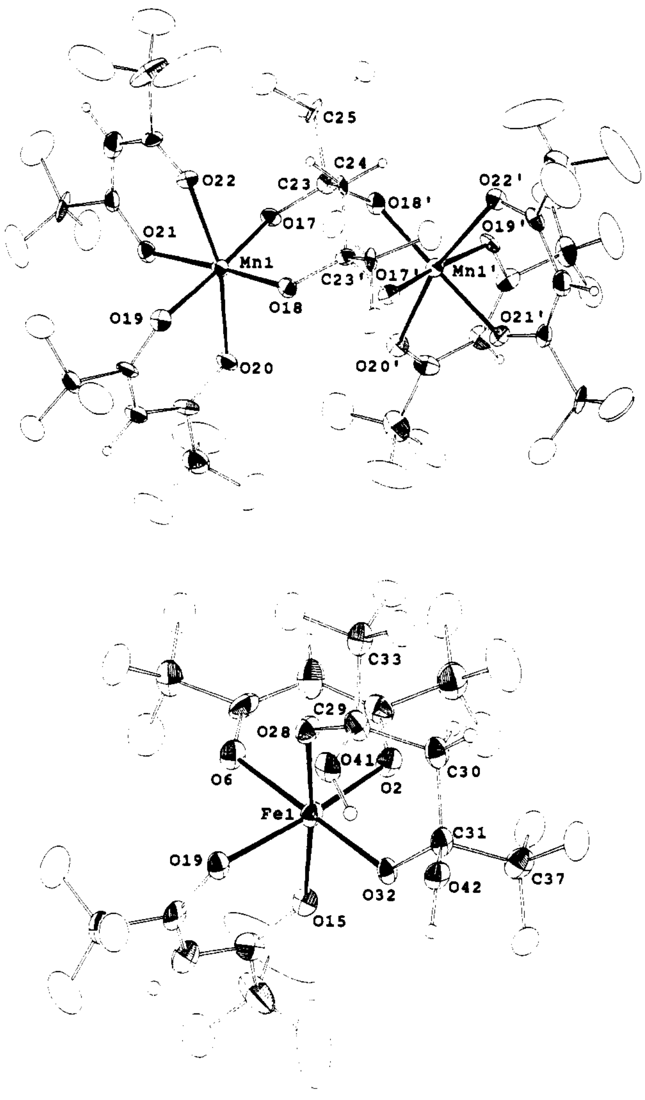

Figure 2. Structures of the dinuclear anion of complex **10** (top) and the mononuclear anion of complex **11** (bottom). For the latter, only one of the two independent anions in the asymmetric unit is shown. Selected distances (Å) for **10**: Mn1–O17, 1.875 (7); Mn1–O18, 1.859 (8); Mn1–O19, 2.017 (7); Mn1–O20, 2.219 (8); Mn1–O21, 1.972 (7); Mn1–O22, 2.228 (8), O17–C23, 1.393 (13); O18–C23′, 1.372 (13); C23–C24, 1.522 (14); C23–C25, 1.547 (16). Selected distances (Å) for **11**: Fe1–O2, 2.048 (4); Fe1–O6, 2.069 (4); Fe1–O15, 2.058 (5); Fe1–O19, 2.048 (4); Fe1–O28, 1.936 (5); Fe1–O32, 1.905 (4); O28–C29, 1.389 (8); O32–C31, 1.382 (8); C29–C30, 1.535 (10); C30–C31, 1.536 (10).

In summary, a convenient synthesis of $hfptH_4$ (**5**) is reported together with its employment to prepare Mn^{III}_2 and Fe^{III} complexes. Two different ligation modes have already been observed, one bridging and one terminal, and others are clearly possible. In its bridging mode in **10**, the ligand supports weak ferromagnetic exchange interactions between Mn^{III} centers. It is clear that the tetraol and bis(*gem*-diol) nature of **5** make it a versatile new ligand for use with a variety of metals and for a variety of objectives/advantages, including variable denticity levels, bridging vs terminal modes, possible high-nuclearity aggregate formation and/or the linking of aggregates into polymeric arrays, and ferromagnetic exchange interactions. The highly fluorinated nature suggests that neutral metal complexes may also prove volatile. Such matters are currently under further investigation.

---

(15) Crystal data for **10**: $C_{35}H_{18}F_{30}N_2O_{12}Mn_2$, 1338.36 g mol^{-1}, monoclinic, $C2/c$, $a = 17.884$ (5) Å, $b = 12.573$ (3) Å, $c = 23.715$ (7) Å, $\beta = 107.77$ (1)°, $V = 5077.62$ Å^3, $Z = 4$, $D_c = 1.75$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $T = -130$ °C, $6° \leq 2\theta \leq 45°$, and R (R_w) = 9.80 (9.37) for 2255 reflections with $F > 2.33\sigma(F)$. The structure was solved by direct methods (MULTAN) and standard Fourier methods. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions. Crystal data for **11**: $C_{20}H_{12}F_{18}NO_8Fe$, 792.13 g mol^{-1}, triclinic, $P\bar{1}$, $a = 14.765$ (3) Å, $b = 18.107$ (3) Å, $c = 11.490$ (4) Å, $\alpha = 92.72$ (2)°, $\beta = 108.46$ (2)°, $\gamma = 78.61$ (2)°, $V = 2856.02$ Å^3, $Z = 4$, $D_c = 1.842$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $T = -167$ °C, $6° \leq 2\theta \leq 45°$, and R (R_w) = 5.63 (5.99) for 5159 reflections with $F > 2.33\sigma(F)$. The structure was solved as above. All non-hydrogen atoms were readily located and refined anisotropically. All hydrogen atoms were clearly visible in a difference Fourier map phased on the non-hydrogen atoms. They were included in the final refinement cycles with isotropic thermal parameters.

(16) The CF_3 fluorine atoms displayed rather large thermal parameters attributable to rotational disorder. This is a common problem with these groups and is a major cause of the fairly high discrepancy indices R and R_w.

Acknowledgment. This work was supported by NIH Grants GM39083 (G.C.) and HL13652 (D.N.H.). E.B. thanks NATO for a postdoctoral fellowship. We thank Sheyi Wang for figure preparation.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters for complexes **10** and **11** and a figure showing effective magnetic moment vs temperature plots for **10** (8 pages). Ordering information is given on any current masthead page.