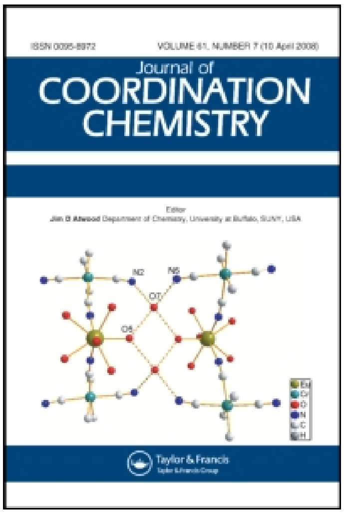

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SYNTHESIS AND CHARACTERIZATION OF POLYFLUORINATED β-DIKETONATE TRANSITION METAL COMPLEXES[1,2]

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SYNTHESIS AND CHARACTERIZATION OF POLYFLUORINATED β-DIKETONATE TRANSITION METAL COMPLEXES[1,2]

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The preparations of 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione (tdfH) and the Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) metal complexes of its monoanion (tdf) are described. The metal complexes have been characterized by elemental analysis, IR and visible spectroscopies, magnetic moment for the paramagnetic compounds, and ^1H and ^{19}F NMR spectroscopy for the Zn(II) and Pd(II) complexes. X-ray structural studies of $Cu(tdf)_2 \cdot C_2H_5OH$, $Cu(tdf)_2 \cdot 2H_2O$, and $Mn(tdf)_2 \cdot 2H_2O$ were undertaken. The geometry of the Cu(II) ethanolate complex is square pyramidal, while the Cu(II) dihydrate complex is distorted octahedral with the two aquo ligands occupying *trans* coordination sites. The Mn(II) dihydrate complex appears also to have distorted octahedral geometry with the two aquo ligands situated *cis* to each other.

KEYWORDS: Volatile metal complexes; fluorinated β-diketones; CVD precursors

INTRODUCTION

Identification and characterization of volatile source materials for chemical vapor deposition (CVD) of device-quality metallization layers has been an area of intense research.[3] Suitable precursors for CVD processes ideally possess specific properties including appreciable vapor pressures in order to facilitate rapid delivery to the substrate. The precursor also must undergo facile decomposition at the target to give the desired material layer with stable, volatile byproducts that can be cleanly swept from the vicinity of the deposition. In addition, the ease of handling of a CVD source, while not necessarily a paramount consideration, is important. A precursor that is stable to ambient temperature and atmospheric conditions is highly desirable, since such a compound can be handled without costly or specialized equipment.

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In particular, metal complexes containing ancillary ligands of the β-diketonate type have been found to be extremely useful as chemical vapor deposition precursors for various metal, ceramic, and insulator phases[4–7] due to the significant volatility of this class of compounds.[8] It has previously been observed that increasing either the steric bulk or the degree of fluorination of the peripheral substituents of the β-diketonate ligand leads to greater volatility of the metal complex.[8] Presumably the former effect minimizes the tendency of these complexes to dimerize or aggregate in the solid, while the latter effect increases coulombic repulsions and reduces van der Waals attractions between complexes. We reasoned that β-diketonate metal complexes containing two n-C_3F_7 peripheral side chains might have both of these benefits. Herein, we report on the synthesis of the β-diketone, 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione (tdfH). We have also prepared and characterized $M(tdf)_2 \cdot nH_2O$ (M = Mn, Co, Ni, Cu, Zn, n = 2,; M = Pd, n = 0), as well as $Cu(tdf)_2 \cdot C_2H_5OH$, $Mn(tdf)_2 \cdot H_2O \cdot C_2H_5OH$, and $Fe(tdf)_3 \cdot 2H_2O$. Solid state structures of $Cu(tdf)_2 \cdot C_2H_5OH$ and $M(tdf)_2 \cdot 2H_2O$ (M = Cu or Mn) have been determined.

At the time that we initiated our studies of the tdf ligand in the spring of 1991, we were aware of only two previous reports regarding metal complexes of this ligand. These involved the utilization of $Eu(tdf)_3$ as a lanthanide shift reagent for ^1H NMR spectroscopy.[9,10] Indeed, there were indications from this work that the n-C_3F_7 group was significantly bulkier than the t-C_4H_9 group.[10] While our work was in progress, we note that several other contributions to the coordination chemistry of the tdf ligand have appeared. Fragala and coworkers have reported on a preparation of tdfH, as well as on the use of $Ba(tdf)_2 \cdot$tetraglyme as a barium source for CVD of $BaPbO_3$.[11] In a series of articles, Cole-Hamilton, Hitchman and coworkers have reported on a synthesis of tdfH, the preparation of tdf metal complexes of Ca(II), Sr(II), Ba(II), Y(III), and Cu(II), including the solid state structure of $Cu(tdf)_2 \cdot C_2H_5OH$, and the CVD of BaF_2 using derivatives of $Ba(tdf)_2$.[7,12–14]

EXPERIMENTAL SECTION

Materials and Methods

Electronic spectra were determined on dilute $CHCl_3$ solutions containing 0.75% C_2H_5OH using a Shimadzu UV-160 spectrophotometer at ambient temperature. Molar absorptivity coefficients are reported in mol^{-1} dm^{-3} cm^{-1}. Room temperature (296 K) magnetic susceptibilities were measured for solid samples on a Johnson-Matthey susceptometer. Magnetic moments were calculated using literature diamagnetic corrections.[15] IR spectra were recorded from compressed KBr pellets using a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H and ^{19}F NMR spectra were obtained on a Varian XL-300 spectrometer at 299.943 and 282.203 MHz, respectively. Spectra obtained in $CDCl_3$ solution were referenced to internal $(CH_3)_4Si$ (^1H) or internal $CFCl_3$ (^{19}F). All melting points are uncorrected. Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, Georgia). All yields of the metal complexes in the following synthetic procedures are reported relative to the limiting reagent, methyl heptafluoropropyl ketone (PCR, Inc.).

Preparation of $Cu(tdf)_2 \cdot C_2H_5OH$ *and* $Cu(tdf)_2 \cdot 2H_2O$

The initial stages of this synthesis were performed using standard Schlenk and glovebox techniques. A Schlenk flask attached to a pressure equalizing dropping funnel fitted with a three way stopcock adapter, was charged with sodium methoxide (2.39 g, 44 mmol). The apparatus was connected to an oil bubbler and argon was slowly passed through the apparatus *via* the adapter. Dry diethyl ether (44 mL) was added to the flask and the suspension was stirred and cooled in an ice bath. A solution of ethyl heptafluorobutyrate (10.6 g, 44 mmol) in dry diethyl ether (10 mL) was placed in the dropping funnel and added to the flask at a rate of *ca.* 1 drop per 2 seconds. After the addition was complete, the dropping funnel was rinsed with dry diethyl ether (5 mL). Then, methyl heptafluoropropyl ketone (6.82 g, 32 mmol) in dry diethyl ether (10 mL) was placed in the dropping funnel. This solution was added at the same dropping rate as the ester above and the funnel was rinsed similarly with diethyl ether (5 mL) after the addition. The resulting mixture was stirred at 0–5°C for 24 h, then at room temperature for another 24 h, whereupon the flask was opened to air and its contents transferred to a separatory funnel. A solution of acetic acid (3.04 g) in water (11 mL) was added and the mixture was shaken well. We note that, at this stage of the preparation, the ethereal solution of the tdfH ligand can be separated and stored in a refrigerator for later use (*vide infra*).

For the copper complexes, however, we generally used freshly prepared ligand. Proceeding from above, the ethereal solution of the tdfH ligand was separated from the aqueous layer. Then, copper acetate monohydrate (3.20 g, 16 mmol) dissolved in water (32 mL) was added to the solution of the ligand in a separatory funnel, followed by vigorous shaking. The aqueous layer was separated and the organic layer was washed with water (15 mL). The organic layer was separated, dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue was transferred to a beaker using a small amount of diethyl ether. Upon standing, crude green product slowly crystallized.

The crude product could be recrystallized from either $CHCl_3$ to which a few drops of ethanol were added or CH_2Cl_2 (22–25 mL of either solvent per gram of crude material). From the ethanolic $CHCl_3$, dark green needles were obtained which analyzed as the ethanol solvate of $Cu(tdf)_2$, $Cu(tdf)_2 \cdot C_2H_5OH$. *Anal.* Calcd. for $C_{20}H_8O_5F_{28}Cu$(%): C, 26.00; H, 0.87. Found: C, 25.83; H, 0.88. m.p. 78–80°C; μ_{eff} = 1.9 BM; VIS ($CHCl_3$): λ_{max} 677 (ε 50); IR (KBr): 3583 (m), 1640 (s), 1598 (w), 1540 (s), 1522 (w), 1484 (s), 1350 (s), 1228 (br,s), 1188 (s), 1144 (m), 1120 (s), 968 (m), 952 (m), 932 (s), 878 (m), 800 (s), 760 (m), 752 (m), 684 (m), 644 (m), 550 (m), 531 (m).

From CH_2Cl_2, a light green powder was obtained that analyzed as the dihydrate of $Cu(tdf)_2$, $Cu(tdf)_2 \cdot 2H_2O$. *Anal.* Calcd. for $C_{18}H_6O_6F_{28}Cu$(%): C, 23.66; H, 0.66. Found: C, 23.50; H, 0.73. m.p. 106–109°C; μ_{eff} = 1.9 BM; VIS ($CHCl_3$): λ_{max} 677 (ε 50); IR (KBr): 3578 (br), 1640 (s), 1601 (w), 1540 (s), 1521 (w), 1484 (s), 1350 (s), 1226 (br,s), 1191 (s), 1146 (m), 1120 (s), 968 (m), 952 (m), 932 (s), 878 (m), 800 (s), 760 (m), 754 (m), 686 (m), 646 (m), 548 (m), 535 (m).

Yields of recrystallized product from either solvent system were 60–76%. Similar yields of the copper complexes have been obtained for scale-ups of the reaction as high as 25.0 g of the starting ketone.

Preparation of $Ni(tdf)_2 \cdot 2H_2O$

The nickel complex was prepared by the same method as $Cu(tdf)_2 \cdot 2H_2O$ on half the scale as above (16 mmol of ketone), except that nickel acetate tetrahydrate (1.99 g, 8 mmol) was utilized. The crude product was recrystallized from CH_2Cl_2 to give a light green powder (5.67 g, 78%). *Anal.* Calcd. for $C_{18}H_6O_6F_{28}Ni$(%): C, 23.79; H, 0.67. Found: C, 24.01; H, 0.80. m.p. 164–167°C; μ_{eff} = 3.4 BM; VIS ($CHCl_3$): λ_{max} 645 (ε 15); IR (KBr): 3533 (br), 1640 (s), 1595 (w), 1536 (s), 1515 (w), 1490 (s), 1350 (s), 1224 (br,s), 1188 (s), 1145 (m), 1118 (s), 966 (m), 949 (m), 932 (s), 880 (m), 798 (s), 760 (m), 752 (m), 682 (m), 648 (m), 544 (m), 529 (m).

Preparation of $Co(tdf)_2 \cdot 2H_2O$

The cobalt complex was prepared by the same method as $Cu(tdf)_2 \cdot 2H_2O$ on half the scale (16 mmol of ketone), except that cobalt acetate tetrahydrate (1.99 g, 8 mmol) was utilized. The crude product was recrystallized from CH_2Cl_2 to give a light orange powder (5.62 g, 77%). *Anal.* Calcd. for $C_{18}H_6O_6F_{28}Co$(%): C, 23.78; H, 0.67. Found: C, 23.87; H, 0.84. m.p. 152–154°C; μ_{eff} = 5.2 BM; VIS ($CHCl_3$): λ_{max} 489 (ε 70), 509 (ε 65), 544 (sh); IR (KBr): 3527 (br), 1638 (s), 1596 (w), 1536 (s), 1515 (w), 1486 (s), 1350 (s), 1224 (br,s), 1190 (s), 1144 (m), 1118 (s), 966 (m), 948 (m), 932 (s), 878 (m), 798 (s), 760 (m), 752 (m), 678 (m), 646 (m), 544 (m), 529 (m).

Preparation of $Mn(tdf)_2 \cdot C_2H_5OH \cdot H_2O$

A stored ethereal solution of tdfH, prepared as in the syntheses of the copper complexes (*vide supra*) and nominally containing 20 mmol of ligand, was shaken with an aqueous solution of manganese acetate tetrahydrate (2.45 g, 10 mmol). The crude orange colored product was dissolved in the minimum amount of refluxing $CHCl_3$. The hot solution was cooled to room temperature and then to 0°C to afford bright yellow needles (4.25 g, 46%). *Anal.* Calcd. for $C_{20}H_{10}O_6F_{28}Mn$(%): C, 25.74; H, 1.08. Found: C, 25.34; H, 1.13. m.p. 149–152°C; μ_{eff} = 5.9 BM; IR (KBr): 3492 (br), 1642 (s), 1598 (w), 1536 (s), 1518 (w), 1470 (s), 1348 (s), 1224 (br,s), 1185 (s), 1145 (m), 1122 (s), 966 (m), 949 (m), 928 (s), 878 (m), 798 (s), 758 (m), 748 (m), 732 (m), 674 (m), 632 (m), 591 (m), 542 (m), 529 (m).

Slow recrystallization of $Mn(tdf)_2 \cdot C_2H_5OH \cdot H_2O$ from either $CHCl_3$/heptane or ethanol/H_2O gave pale yellow needles of a complex that appears from X-ray diffraction studies to be best formulated as $Mn(tdf)_2 \cdot 2H_2O$. *Anal.* Calcd. for $C_{18}H_6O_6F_{28}Mn$(%): C, 23.89; H, 0.67. Found: C, 23.54; H, 0.99.

Preparation of $Zn(tdf)_2 \cdot 2H_2O$

A stored ethereal solution of tdfH, prepared as in the syntheses of the copper complexes (*vide supra*) and nominally containing 15 mmol of ligand, was concentrated to the crude ligand by removing the diethyl ether *in vacuo*. The residue was dissolved in water (10 mL) containing NaOH (0.60 g, 15 mmol). To this solution was added a solution of zinc sulfate (1.21 g, 7.5 mmol) in water (10 mL). A light yellow precipitate formed immediately. The reaction mixture was stirred for an hour and then filtered. The crude product was washed with copious amounts of water to give an off-white powder (5.54 g, 81%), that was not recrystallized. *Anal.* Calcd. for $C_{18}H_6O_6F_{28}Zn$(%): C, 23.61; H, 0.66. Found: C, 23.88; H, 0.77. m.p. 119–122°C; ^{1}H NMR ($CDCl_3$): δ 5.72 (s, 1 H, C(O)CHC(O)); ^{19}F NMR ($CDCl_3$): −80.8 (t, 3 F, CF_3, ^4J(F-F) = 8.8 Hz), −118.1 (ABX_3, 2 F, $CF_2CF_2CF_3$, ^2J(F-F) = 296 Hz, ^4J(F-F) = 8.8 Hz), −126.5 (br s, 2 F, $CF_2CF_2CF_3$); IR (KBr): 3537 (br), 1644 (s), 1597 (w), 1540 (s), 1517 (w), 1490 (s), 1350 (s), 1224 (br,s), 1190 (s), 1144 (m), 1118 (s), 964 (m), 949 (m), 930 (s), 878 (m), 800 (s), 760 (m), 753 (m), 678 (m), 644 (m), 544 (m), 529 (m).

Preparation of $Fe(tdf)_3 \cdot 2H_2O$

A stored ethereal solution of tdfH, prepared as in the syntheses of the copper complexes (*vide supra*) and nominally containing 15 mmol of ligand, was concentrated to the crude ligand by removing the diethyl ether *in vacuo*. Iron(II) sulfate heptahydrate (2.1 g, 7.5 mmol) was dissolved in water (20 mL) and the crude tdfH was added. A violet precipitate formed immediately. The precipitate was collected by filtration, washed with cold water, and air dried. The crude product was recrystallized from $CHCl_3$ as for the manganese complex (*vide supra*) to give a maroon powder (3.17 g, 48%). *Anal.* Calcd. for $C_{27}H_7O_8F_{42}Fe$(%): C, 24.70; H, 0.54. Found: C, 24.48; H, 0.48. m.p. 135–139°C; μ_{eff} = 5.7 BM; VIS ($CHCl_3$): λ_{max} 386 (ε 1000), 495 (ε 900); IR (KBr): 3520 (br), 1624 (m), 1604 (m), 1540 (s), 1521 (m), 1462 (s), 1348 (s), 1226 (br,s), 1190 (s), 1143 (m), 1118 (s), 964 (m), 949 (m), 930 (s), 878 (m), 808 (s), 759 (m), 752 (m), 676 (m), 632 (m), 612 (m), 546 (m), 532 (m).

Preparation of $Pd(tdf)_2$

A stored ethereal solution of tdfH, prepared as in the syntheses of the copper complexes (*vide supra*) and nominally containing 5 mmol of ligand, was concentrated to the crude ligand by removing the diethyl ether *in vacuo*. The residue was dissolved in water (5 mL) containing NaOH (0.20 g, 5 mmol). To this solution was added a solution of sodium tetrachloro-palladate (0.74 g, 2.5 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 3 h, then allowed to sit overnight. The precipitated solid was collected on a filter and air dried. The crude product was taken up in a minimum amount of CH_2Cl_2 and filtered. Upon concentration, the amber filtrate gave 0.90 g (39%) of yellow product. *Anal.* Calcd. for $C_{18}H_2O_4F_{28}Pd$(%): C, 23.49; H, 0.22. Found: C, 23.68; H, 0.33. m.p. 51–53°C; ^{1}H NMR ($CDCl_3$): δ 6.46 (s, 1 H, C(O)CHC(O)); ^{19}F NMR ($CDCl_3$): −81.0 (t, 3 F, CF_3, ^4J(F-F) = 8.8 Hz), −118.1 (q, 2 F, $CF_2CF_2CF_3$, ^4J(F-F) = 8.8 Hz), −126.8 (s, 2 F, $CF_2CF_2CF_3$); IR (KBr): 1654 (s), 1596 (s), 1536 (s), 1522 (s), 1438 (s), 1348 (s), 1232 (br,s), 1195 (s), 1171 (m), 1122 (s), 965 (m), 936 (s), 876 (m), 810 (m), 758 (m), 750 (m), 712 (m), 652 (m), 625 (m), 552 (m), 538 (m).

X-ray crystallography

$Cu(tdf)_2 \cdot C_2H_5OH$, Mol. wt 923.8, triclinic, space group $P\bar{1}$ (no. 2), Z = 2, a = 11.256(3) Å, b = 12.347(3) Å, c = 12.916(4) Å, α = 97.00(2)°, β = 108.89(2)°, γ = 109.61(2)°, V = 1545.3(7) Å^3, D_{calc} = 1.99 g cm^{-3}, $F(000)$ = 898, μ = 9.0 cm^{-1}.

A well-formed light green prism of Cu(tdf)$_2\cdot C_2H_5OH$ was mounted on the tip of a glass capillary with epoxy. Axial photographs indicated the triclinic crystal system. Unit cell parameters were determined from 25 well-centered, intense reflections in the range 18 $\leq 2\Theta \leq 25°$.

A Siemens R3m diffractometer in the $\Theta/2\Theta$ mode with variable scan speed (3 to 20 deg min^{-1}) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å) was used to measure 5476 unique reflections with 3 $\leq 2\Theta \leq 50°$ (h, k, l = ±13, ±15, 16) at ambient temperature. Of these, there were 2550 reflections with $|F_o| > 4|F_o|$ No decay was observed over the course of the data collection. Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption.[16] Heavy atoms were located *via* Patterson maps and full-matrix least-squares refinement was accomplished with the SHELXTL Plus package of programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically, fixed at a C-H distance of 0.96 Å, and not refined. The structure was refined to R = 0.076, R_w = 0.077 (data: parameter = 6.6; g = 0.002; see ref. 16) and R = 0.16 for all 5476 data.

Cu(tdf)$_2\cdot 2H_2O$, Mol. wt 913.8, monoclinic, space group *C*2/*c* (No. 15), Z = 4, a = 24.881(8) Å, b = 5.554(2) Å, c = 22.044(7) Å, β = 96.90(3)°, V = 3024(2) Å^3, D_{calc} = 2.01 g cm^{-3}, $F(000)$ = 1772, μ = 9.2 cm^{-1}.

A light green needle of Cu(tdf)$_2\cdot 2H_2O$ was mounted on the tip of a glass capillary with epoxy. Axial photographs indicated the monoclinic crystal class. Determination of unit cell parameters, data collection and structure solution, and refinement methods were the same as above for Cu(tdf)$_2\cdot C_2H_5OH$, with the following changes. The $\omega/2\Theta$ mode was used to measure 2693 unique reflections with 3 $\leq 2\Theta \leq 50°$ (h, k, l = ±28, 6, 26) at ambient temperature, with 1517 reflections having $|F_o| > 4|F_o|$. The space group was determined to be *C*2/*c* (no. 15) rather than *Cc* (no. 9) *via* successful solution in the former. The choice of the centrosymmetric space group necessitates that the complexes occupy special positions; the Cu atom was located on a center of symmetry at (1/4, 1/4, 0). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as above. The structure was refined to R = 0.093, R_w = 0.096 (data:parameter = 6.3; g = 0.0004; see ref. 16) and R = 0.14 for all 2693 data.

Mn(tdf)$_2\cdot 2H_2O$, Mol. wt 905.1, monoclinic, space group *C*2/*c* (no. 15), Z = 4, a = 26.207(8) Å, b = 12.230(5) Å, c = 10.050(5) Å, β = 104.33(3)°, V = 3121(2) Å^3, D_{calc} = 1.93 gm cm^{-3}, $F(000)$ = 1756, μ = 9.2 cm^{-1}.

A light yellow needle of Mn(tdf)$_2\cdot 2H_2O$ was mounted on the tip of a glass capillary with epoxy. Axial photographs indicated the monoclinic crystal class. Determination of unit cell parameters, data collection and structure solution, and refinement methods were the same as above for Cu(tdf)$_2\cdot C_2H_5OH$ with the following changes. The $\omega/2\Theta$ mode was used to measure 2342 unique reflections with 3 $\leq 2\Theta \leq 50°$ (h, k, l = ±31, 14, 12) at ambient temperature, with 1228 reflections having $|F_o| > 4|F_o|$ Statistical analysis of the data indicated that the correct space group was *C*2/*c* (no. 15) rather than *Cc* (no. 9). The choice of the centrosymmetric space group necessitates that the complexes occupy special positions; the Mn atom was located on the two-fold rotational axis at (0, y, 1/4). However, poor crystal quality, which limited the amount of data, combined with disorder of the C_3F_7 chains, prevented complete refinement of the data to convergence. Fragala and coworkers encountered similar problems in the structure solution of $Ba(tdf)_2 \cdot$tetraglyme.[11] Attempts to solve the structure in *Cc* were not successful at all.

RESULTS AND DISCUSSION

Synthesis of tdfH and the Copper Complexes

The β-diketone, tdfH, was prepared by the addition of methyl heptafluoropropyl ketone to *excess* ethyl heptafluorobutyrate in diethyl ether solution in the presence of sodium methoxide. When freshly prepared ethereal solutions of tdfH were acidified with acetic acid and shaken with aqueous copper(II) acetate, the organic phase turned deep green in colour. After separation, the organic layer provided the crude Cu(II) complex, which could be made analytically pure by recrystallization from either commercial $CHCl_3$ or CH_2Cl_2 in good, overall yields (60–76%) based upon the limiting reagent, methyl heptafluoropropyl ketone. From ethanolic $CHCl_3$, we obtained the ethanol solvate, $Cu(tdf)_2 \cdot C_2H_5OH$, while the material that crystallized from CH_2Cl_2 was the dihydrate, $Cu(tdf)_2 \cdot 2H_2O$.

Cole-Hamilton's synthesis[12] of tdfH parallels the method reported here. The condensation of the fluorinated ester and ketone was effected in dry petroleum and the tdfH was ultimately separated from the reaction mixture as the monohydrate complex, $Cu(tdf)_2 \cdot H_2O$.[12] These workers then proceeded to isolate pure tdfH in 32% yield *via* acidification of a solution of the copper complex, followed by distillation. The main difference in the two preparations of tdfH is found in the mole ratio of ketone to ester employed in the condensation step. Cole-Hamilton's reported method utilized a ratio of 1.15 to 1.00.[12] We have found that the final yield of pure copper complex (60–76%), prepared in *situ* from ethereal solutions of tdfH (*vide supra*), is maximized when the mole ratio of ketone to ester is 1.00:1.38. Assuming approximate similarity in yields of tdfH, we feel that our method results in more efficient usage of the fluorinated starting materials, since the ketone is considerably more expensive than the ester.

Fragala and coworkers' method[11] for the preparation of tdfH again bears some similarity to our procedure. Sodium hydride was substituted for sodium methoxide to accomplish the condensation reaction using a ketone:ester mole ratio of 1.00:1.00. The tdfH then was isolated directly from the reaction mixture in 53% yield, which is an advantage for the preparation of alkaline earth metal derivatives of tdf.[11,12]

Synthesis of the Other Metal Complexes

The complexes $Mn(tdf)_2 \cdot C_2H_5OH \cdot H_2O$ and $M(tdf)_2 \cdot 2H_2O$ (M = Mn, Co, Ni) were prepared by a method that was analogous to that which we employed for the copper compounds by simply substituting the appropriate divalent metal acetate into the procedure. For Fe, Zn, and Pd, a modification of our basic synthetic approach was required. Concentration of the ethereal solution of the ligand provided crude tdfH. Addition of either neat crude tdfH (for Fe) or a basic aqueous solution of tdf (for Zn and Pd) to an aqueous solution of an appropriate metal(II) salt, gave $Fe(tdf)_3 \cdot 2H_2O$, $Zn(tdf)_2 \cdot 2H_2O$, and $Pd(tdf)_2$ respectively (see the Experimental section). Facile oxidation of Fe(II) to Fe(III) occurred during the formation of $Fe(tdf)_3 \cdot 2H_2O$, as anticipated.[17–19]

Physical Characterization of the Metal Complexes

The new complexes have relatively low melting points (see Experimental Section). The melting points of $M(tdf)_2 \cdot 2H_2O$ (M = Co, Ni, Cu, and Zn) are 20 to 40°C lower than those of the corresponding hfa (hfa = the monoanion of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) complexes.[20,21]

IR spectra for the complexes with the central metal ion in the + 2 oxidation state, M(II), were rather similar from compound to compound (see Experimental section). All, except the Pd(II) complex, had evidence for the presence of coordinated, hydroxylated solvent molecules in the expected region of the spectrum and only minor differences were evident in the fingerprint region. The region that is diagnostic for β-diketonate stretches (1475–1700 cm^{-1}) contained three strong bands at slightly lower energies than for hfa complexes.[20,22] The Fe(III) tdf complex had an IR spectrum that was analogous to those for the M(II) complexes except that the double bonded region of the spectrum contained five medium to strong bands.

The room temperature magnetic moments for the new paramagnetic tdf metal complexes were all within ranges expected for monomeric, mononuclear, high-spin metal complexes and very close to those measured for other β-diketonate complexes of Cu(II),[21] Ni(II),[23,24] Co(II),[25] Mn(II),[26,27] and Fe(III).[28,29]

The visible spectra for $Cu(tdf)_2 \cdot C_2H_5OH$ and $M(tdf)_2 \cdot 2H_2O$ (M = Cu, Ni, or Co) all display weak absorptions at energies in accordance with monomeric, octahedral or square pyramidal geometries.[21,24,25,30,31] The Zn(II) (d^{10}), Mn(II) (high-spin d^5), and Pd(II) (presumably square planar, low-spin d^8) tdf complexes had no maxima in the visible absorption range. Although also high-spin d^5, the Fe(III) tdf complex had two moderately strong charge-transfer bands in the visible region, as observed for other tris(β-diketonate) Fe(III) complexes.[32]

In summary, the spectroscopic data (IR, μ_{eff}, VIS) strongly suggest that the Cu(II), Ni(II), Co(II), Mn(II), and Fe(III) tdf complexes are monomeric, mononuclear complexes. Given the known proclivity of bis(hfa) metal complexes toward coordination of solvent molecules,[39] we believe that the new tdf complexes of type $M(tdf)_2 \cdot 2L$ (where M is one of the above metal ions complexes of type $M(tdf)_2 \cdot 2L$ (where M is one of the above metal ions and L is either H_2O and/or C_2H_5OH) are likely octahedral, with two coordinated solvent molecules. The exceptions would be $Cu(tdf)_2 \cdot C_2H_5OH$, which is known to be five-coordinate square pyramidal from X-ray studies (ref. 12 and *vide infra*), and $Fe(tdf)_3 \cdot 2H_2O$, which is likely a tris chelate complex that is octahedral, but which does not have any coordinated solvent molecules.

X-ray Diffraction Studies

In order to better describe the geometries of the new tdf complexes, we turned to single crystal X-ray diffraction methods. In these studies, we encountered some of the same difficulties that other workers have noted; viz, poor crystal quality, which limits the amount and quality of data that can be collected, as well as disorder problems in the n-C_3F_7 side chains. We were able to obtain reasonably good single crystals of $Cu(tdf)_2 \cdot C_2H_5OH$, $Cu(tdf)_2 \cdot 2H_2O$, and $Mn(tdf)_2 \cdot 2H_2O$.

We will limit our discussion on the structure of $Cu(tdf)_2 \cdot C_2H_5OH$, since Cole-Hamilton and coworkers have previously reported it.[12] Our numbering scheme for square pyramidal $Cu(tdf)_2 \cdot C_2H_5OH$ is shown in Fig. 1. The plane defined by the four oxygen atoms of the tdf ligands is the basal plane (planar to within ±0.05 Å). The Cu atom is ~0.19 Å above the basal plane toward the apical ethanol ligand. The six-membered rings of the tdf ligands are planar to within ±0.02 Å and form angles of 10.5° and 8.6° to the basal plane. Bond lengths and angles within the coordination sphere (Table 1) and for the ligands are as expected for fluorinated β-diketonate Cu(II) complexes.[33]

In agreement with Cole-Hamilton,[12] we find that two C_3F_7 substituents per molecule, one for each tdf ligand, lie above the four-oxygen basal plane, while the other two C_3F_7 groups lie below it. The packing diagram (Fig. 2) shows that the ethanol ligand is nestled in hydrophobic regions, surrounded by four C_3F_7 groups from pairs of symmetry related molecules. This motif prevents any inter- or intramolecular hydrogen bonding from occurring. The packing diagram also reveals that the molecules arrange themselves into loosely connected dimers with weak Cu(1)···F(2') interactions at the "empty" axial coordination site with a distance of

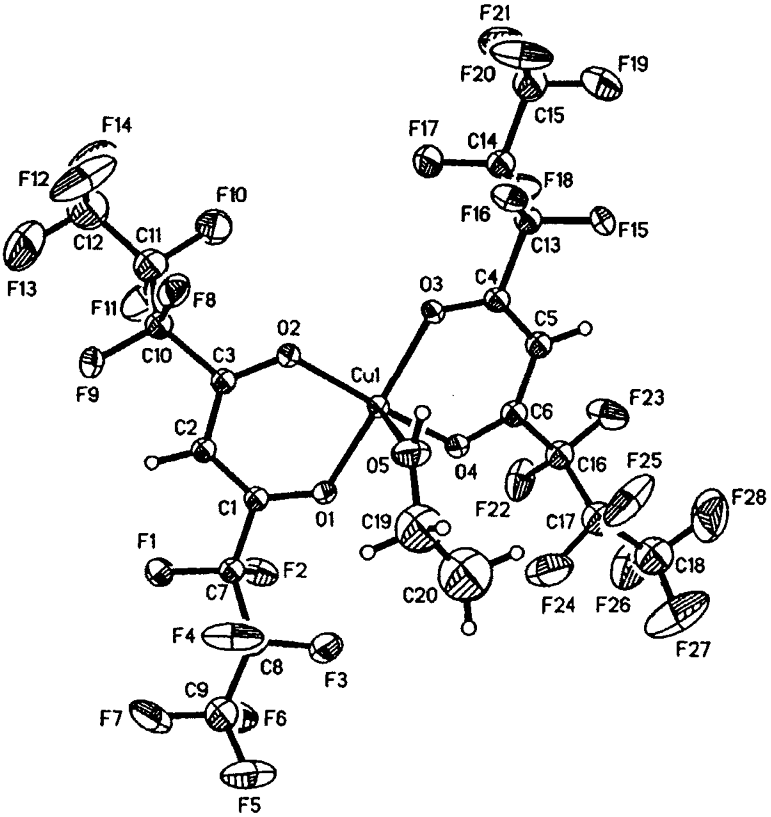

Figure 1 Molecular structure and atom numbering scheme for $Cu(tdf)_2 \cdot C_2H_5OH$ (20% probability ellipsoids).

Table 1 Selected bond lengths (Å) and angles (°) for Cu(tdf)$_2$·C$_2$H$_5$OH

Cu(1)-O(1)	1.923(9)
Cu(1)-O(2)	1.946(5)
Cu(1)-O(3)	1.952(8)
Cu(1)-O(4)	1.930(5)
Cu(1)-O(5)	2.195(10)
O(1)-Cu(1)-O(2)	92.4(3)
O(1)-Cu(1)-O(3)	171.4(3)
O(2)-Cu(1)-O(3)	87.8(3)
O(1)-Cu(1)-O(4)	85.1(3)
O(2)-Cu(1)-O(4)	165.4(3)
O(3)-Cu(1)-O(4)	92.6(3)
O(1)-Cu(1)-O(5)	96.7(4)
O(2)-Cu(1)-O(5)	94.9(3)
O(3)-Cu(1)-O(5)	91.8(3)
O(4)-Cu(1)-O(5)	99.6(3)

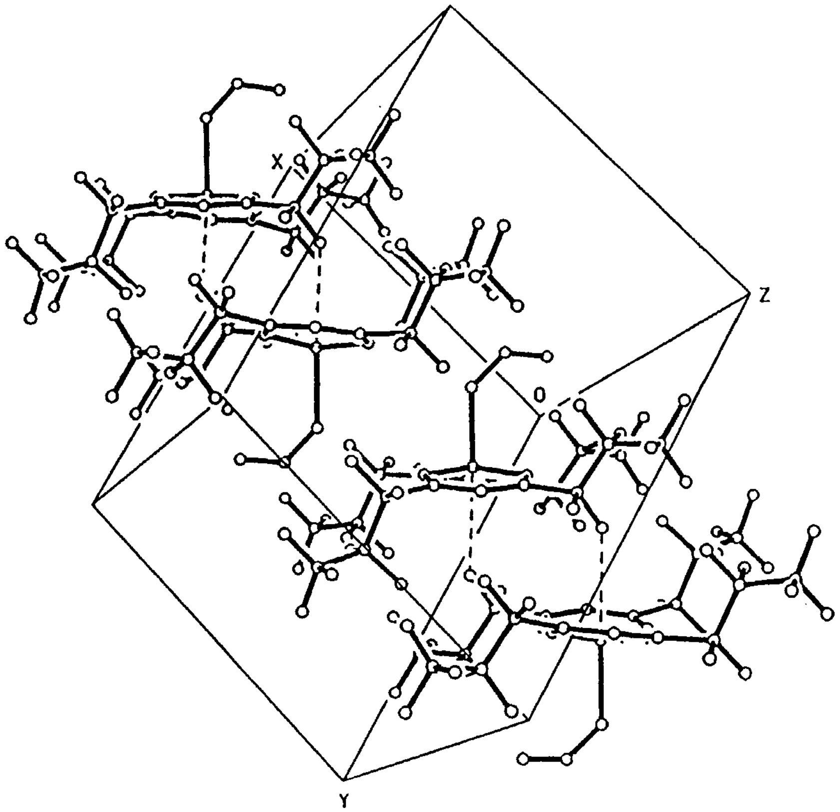

Figure 2 Crystal packing diagram for Cu(tdf)$_2$·C$_2$H$_5$OH. The dotted lines illustrate the weak intermolecular Cu(1)···F(2') contacts (see text).

2.999(8) Å between neighboring molecules.[34] Curiously, the previous structural solution found no intermolecular contacts within 4.0 Å and no significant intermolecular interaction with the sixth coordination site.[12] The net result of the observed distribution of molecular substituents for crystalline $Cu(tdf)_2 \cdot C_2H_5OH$ seems to allow as efficient packing of the molecules as possible, while minimizing unfavorable coulombic repulsions between C_3F_7 groups in neighboring molecules.

The molecular structure of $Cu(tdf)_2 \cdot 2H_2O$ is shown in Fig. 3. This complex crystallizes as long needles, which limited the amount of data that could be collected, and ultimately, the accuracy of the structure determination. The Cu atoms are six-coordinate and positioned on centers of symmetry in the unit cell. As a consequence of this, the Cu atom is crystallographically constrained to be in the plane defined by the four oxygen atoms of the tdf ligands, with the coordinated water molecules occupying *trans* axial positions. The structure is best described as tetragonally-distorted octahedral with elongation along the copper to water bond directions (Table 2). Other bond lengths and angles within the coordination sphere (Table 2) and ligands are as expected.

The packing diagram for $Cu(tdf)_2 \cdot 2H_2O$ is rather more complicated than that for $Cu(tdf)_2 \cdot C_2H_5OH$, with potential intermolecular hydrogen-bonding between the coordinated water ligands and oxygen and fluorine atoms of neighboring molecules

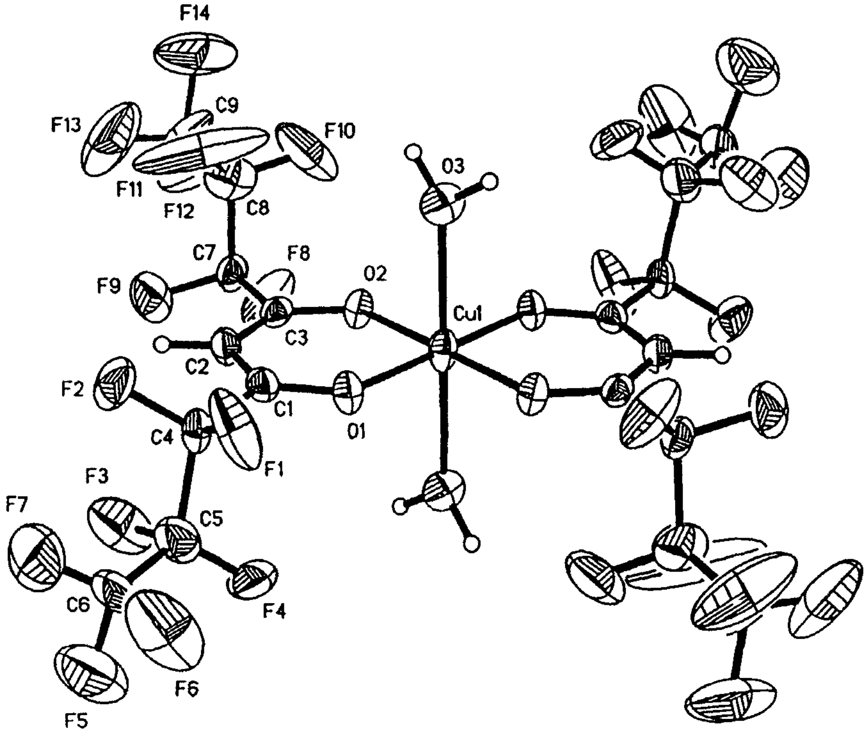

Figure 3 Molecular structure and atom numbering scheme for $Cu(tdf)_2 \cdot 2H_2O$ (20% probability ellipsoids). Unnumbered atoms are related to numbered atoms by the crystallographic center of symmetry on which the Cu atom is situated.

Table 2 Selected bond lengths (Å) and angles (°) for $Cu(tdf)_2 \cdot 2H_2O$[a]

Cu(1)-O(1)	1.941(6)
Cu(1)-O(2)	1.944(7)
Cu(1)-O(3)	2.363(8)
O(1)-Cu(1)-O(2)	92.5(3)
O(1)-Cu(1)-O(3)	89.5(3)
O(2)-Cu(1)-O(3)	90.4(3)
O(1)-Cu(1)-O(2a)	87.6(3)
O(1)-Cu(1)-O(3a)	90.5(3)
O(2)-Cu(1)-O(3a)	89.6(3)

[a] Atoms related by the crystallographic center of symmetry are indicated by the letter "a" affixed to the atom label.

(Fig. 4). The hydrogen-bonding may account for the somewhat higher melting point of $Cu(tdf)_2 \cdot 2H_2O$ compared to $Cu(tdf)_2 \cdot C_2H_5OH$. Interestingly though, the C_3F_7 groups of $Cu(tdf)_2 \cdot 2H_2O$ adopt the same staggered arrangement as for $Cu(tdf)_2 \cdot C_2H_5OH$ (*vide supra*), in which pairs of C_3F_7 groups are alternatively above and below the plane defined by the tdf ligands (Fig. 3). At this time, it is tempting to speculate that this is a recurring motif for axially-symmetric $M(tdf)_2$ complexes, which allows the C_3F_7 groups to minimize coulombic repulsions.

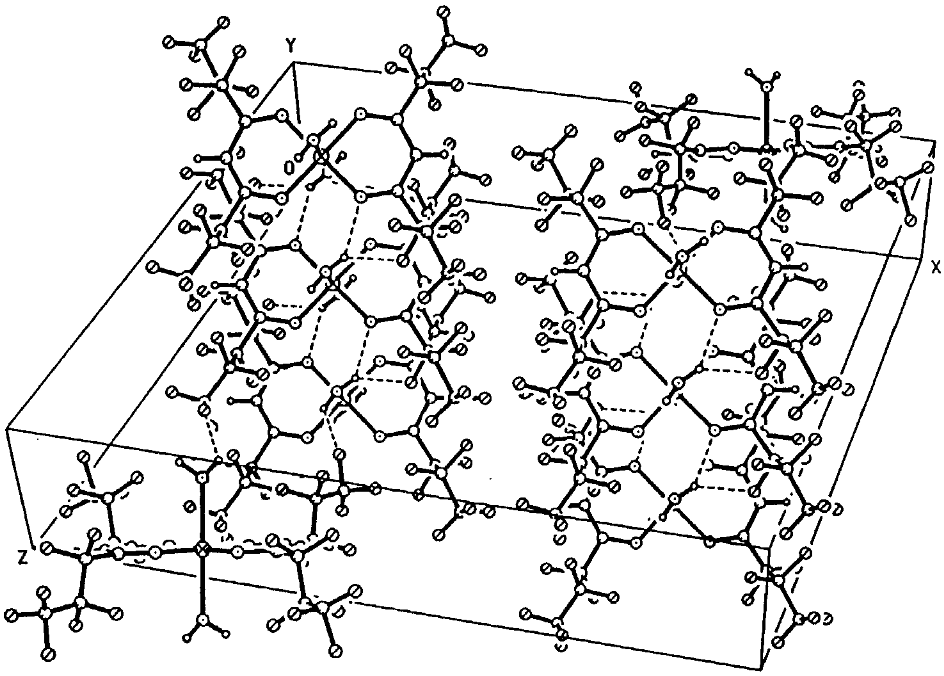

Figure 4 Crystal packing diagram for $Cu(tdf)_2 \cdot 2H_2O$. The dotted lines indicate potential intermolecular hydrogen-bonding interactions.

For further comparison, we wanted crystals of tdf complexes for other transition metals. Like $Cu(tdf)_2 \cdot 2H_2O$, the complex $Mn(tdf)_2 \cdot 2H_2O$ also crystallized as long needles. Unfortunately, the crystal data set was particularly poor. As the refinement proceeded, it became increasingly evident that the C_3F_7 substituents on the tdf ligands were disordered, a problem that also spoiled the structure determination of $Ba(tdf)_2 \cdot$tetraglyme.[11] The paucity of data prevented complete refinement to convergence, but was sufficient to allow us to determine that the geometry about the Mn atom was *cis* octahedral, with both water molecules coordinated to the Mn ion (Fig. 5), rather than *trans* octahedral as found in the Cu case. The Mn-O bond distances at this incomplete level of refinement were in the typical range of 2.10 to 2.20 Å found for Mn(II) β-diketonate complexes.[35–38] Previous structural determinations of $Mn(hfa)_2L_2$ molecules, where L is a nitroxide radical, demonstrated that *cis* or *trans* octahedral structures are found for Mn complexes with fluorinated β-diketonate ligands.[35–38]

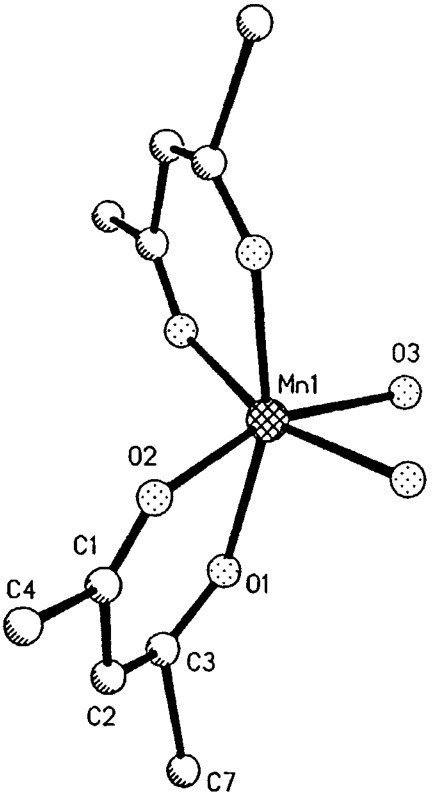

Figure 5 The inner coordination environment of $Mn(tdf)_2 \cdot 2H_2O$.

NMR Studies

The ^1H NMR spectrum of $Pd(tdf)_2$ has a single resonance in $CDCl_3$ solution for the methine group of the tdf ligand at δ 6.46. By comparison, $Pd(hfa)_2$ has methine resonances at δ 6.42 and 6.50 in $CDCl_3$ and CD_3OD solutions, respectively.[39]

The ^{19}F NMR spectrum consists of a triplet at δ −81.0 (^4J(F-F) = 8.8 Hz), a quartet at δ −118.1 (^4J(F-F) = 8.8 Hz), and a singlet at δ -126.8. The above resonances integrate to the ratio 3:2:2. Clearly the furthest downfield resonance, a triplet, is due to the CF_3 group of the tdf ligand based upon the integration. Vicinal ^3J(F-F) coupling constants are often small (<2 Hz) and difficult to measure, while ^4J(F-F) coupling constants are often in the range of 7 to 9 Hz.[40–45] Thus, we assign the furthest upfield resonance, a broadened singlet, to the CF_2 group that is *between* the terminal CF_3 group and the CF_2 group next to the carbonyl substituent of the tdf ligand. Finally, the quartet signal is assigned to the CF_2 group next to the carbonyl group of the tdf ligand. This interpretation for the ^{19}F chemical shift assignments in $Pd(tdf)_2$ is supported by a number of previous studies involving the $CF_3CF_2CF_2C(O)$ moiety.[40,44,45] Thus, we also conclude that there probably should be a reversal of the ^{19}F NMR assignments for the CF_2 resonances of $M(tdf)_2 \cdot H_2O$ (M = Ca, Sr, and Ba).[12] Finally, the ^1H and ^{19}F NMR spectra of $Pd(tdf)_2$ are entirely consistent with square planar geometry, as found for other bis(β-diketonate) complexes of Pd.[39,46]

The similarity of the melting point and IR spectrum of $Zn(tdf)_2 \cdot 2H_2O$ to those of the other M(II) tdf complexes (M = Mn, Co, Ni, Cu) suggests that it too has octahedral geometry. The ^1H NMR spectrum of $Zn(tdf)_2 \cdot 2H_2O$ has a single resonance in $CDCl_3$ solution at δ 5.72 as compared to δ 5.94 for $Zn(hfa)_2 \cdot 2H_2O$ in CH_3OH solution.[47] The ^{19}F NMR spectrum of $Zn(tdf)_2 \cdot 2H_2O$ is of special interest. The spectrum consists of a triplet at δ −80.8 (^4J(F-F) = 8.8 Hz), an ABX_3 pattern (Fig. 6) centered at δ −118.1 (^2J(F-F) = 296 Hz; ^4J(F-F) = 8.8 Hz), and a slightly broadened singlet at δ −126.5. The above resonances integrate to the ratio 3:2:2.

The same arguments as for the Pd complex (*vide supra*) assign the resonance at δ −118.1 to the ^{19}F NMR resonance of the CF_2 group next to the carbonyl moiety. The ABX_3 pattern indicates that the fluorine atoms in this group are diastereotopic and thus, magnetically inequivalent. This situation will arise if (a) the stereochemical configuration of the complex about the Zn center is chiral and (b) the complex is stereochemically rigid on the NMR time scale. Thus, known geometries for Zn nonfluorinated β-diketonate complexes such as tetrahedral,[48] and square pyramidal,[49,50] as well as *trans* octahedral must be ruled out based upon the ^{19}F NMR spectroscopic results since the fluorine atoms in the CF_2 groups would only be enantiotopic for these geometries. The most likely geometry for $Zn(tdf)_2 \cdot 2H_2O$ that would cause diastereotopic fluorine atoms in the CF_2 groups is *cis* octahedral, a geometry that has been observed in an X-ray study of $Zn(hfa)_2(NIT\text{-}iPr)(H_2O)$, where NIT-iPr is a substituted nitroxyl radical.[51]

Interestingly, the CF_2 group in the middle of the *n*-C_3F_7 substituent of the tdf ligand in $Zn(tdf)_2 \cdot 2H_2O$ also nominally has diastereotopic fluorine atoms. However, these fluorine atoms are further from the Zn atom and apparently their magnetic environments are not sufficiently different to cause significantly different chemical shifts. Only a slight broadening of the resonance for the fluorine atoms in this group is observed.

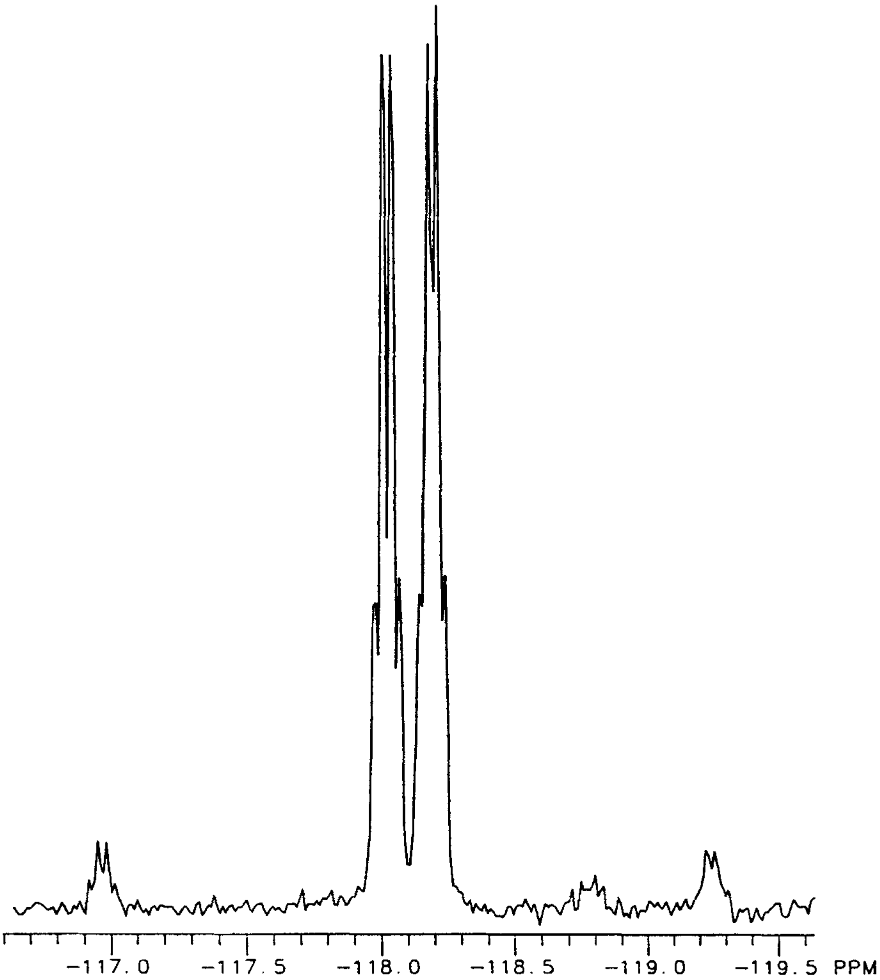

Figure 6 Expansion of the ABX_3 pattern for the ^{19}F NMR spectrum of $Zn(tdf)_2 \cdot 2H_2O$.

SUMMARY

The highly fluorinated β-diketone, tdfH, was synthesized, as well as metal complexes of its anion, tdf, with Cu(II), Mn(II), Co(II), Ni(II), Zn(II), Fe(III), and Pd(II). The metal complexes, $M(tdf)_2 \cdot 2L$ ($L = H_2O$ and/or C_2H_5OH) appear to be octahedral complexes from physical and spectroscopic data, while $Cu(tdf)_2 \cdot C_2H_5OH$ and $Pd(tdf)_2$ are square pyramidal and square planar, respectively. Further, we were able to establish for $M(tdf)_2 \cdot 2H_2O$ that the coordinated water molecules are *trans* for M = Cu and *cis* for M = Mn or Zn.

Prelimary results indicate that the Cu derivatives have significantly higher volatility at temperatures above 60°C than other widely used Cu precursors.[4,52]

Studies are underway to investigate the utility of the new tdf metal complexes for CVD processes.

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