# Decomposition and Cycloaddition Reactions of hfacac and Syntheses and Structures of Ln$^{III}_2$(hfacac)$_4$(bdmap)$_2$(H$_2$O)$_2$(THF)$_2$, Ln$^{III}$Cu$^{II}$(bdmapH)$_2$(hfacac)$_2$(O$_2$CCF$_3$)L, and Ln$^{III}$Cu$^{II}_2$(hfacac)(bdmap)$_3$(O$_2$CCH$_3$)$_2$(O$_2$CCF$_3$)(hfacacH) (Ln = Y, Pr, Nd; hfacac = Hexafluoroacetylacetonato; bdmap = 1,3-Bis(dimethylamino)-2-propanolato; L = 2-Methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato)

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The reactions of Ln(hfacac)$_3$ with the bdmapH ligand and Cu(OCH$_3$)$_2$ or Cu$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$ have been investigated where hfacac = hexafluoroacetylacetonato, bdmapH = 1,3-bis(dimethylamino)-2-propanol. The hfacac ligand in these reactions has been found to undergo decomposition or cycloaddition with 1,1,1-trifluoro-2,2-propanediol. Two dinuclear compounds, Ln$_2$(hfacac)$_4$(bdmap)$_2$(H$_2$O)$_2$(THF)$_2$, (**1**, Ln = Pr) and LnCu(bdmapH)$_2$-(hfacac)$_2$(O$_2$CCF$_3$)L (Ln = Pr, **2a**; Y, **2b**; L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato), have been isolated from the reaction of Ln(hfacac)$_3$ with Cu(OCH$_3$)$_2$ and bdmapH in a 1:1:2 ratio in THF. These two compounds also were obtained by independent syntheses. A trinuclear compound, LnCu$_2$(hfacac)(bdmap)$_3$(O$_2$-CCH$_3$)$_2$(O$_2$CCF$_3$)(hfacacH) (Ln = Nd, **3a**; Pr, **3b**), was obtained from the reaction of Ln(hfacac)$_3$ with Cu$_2$(O$_2$-CCH$_3$)$_4$(H$_2$O)$_2$ and bdmapH in a 1:1:3 ratio in THF. The crystal structures of these compounds have been determined by X-ray diffraction analyses. Their thermal behavior has been examined by themogravimetric analysis. The magnetic properties of compounds **1**, **2b**, and **3b** were examined by EPR and magnetic susceptibility measurements. Crystal data: **1**, triclinic, $P\bar{1}$, $a$ = 12.00(1) Å, $b$ = 13.71(1) Å, $c$ = 11.284(7) Å, $\alpha$ = 112.59(6)°, $\beta$ = 107.06(7)°, $\gamma$ = 97.48(8)°, $V$ = 1575(3) Å$^3$, $d_{calc}$ = 1.57 g cm$^{-3}$, $Z$ = 1; **2a**, monoclinic, $Cc$, $a$ = 18.205(5) Å, $b$ = 18.350(6) Å, $c$ = 15.924(4) Å, $\beta$ = 94.96(2)°, $V$ = 5299(2) Å$^3$, $d_{calc}$ = 1.72 g cm$^{-3}$, $Z$ = 4; **3a**, monoclinic, $P2_1/n$, $a$ = 12.027(4) Å, $b$ = 15.222(4) Å, $c$ = 32.07(2) Å, $\beta$ = 100.13(4)°, $V$ = 5894(5) Å$^3$, $d_{calc}$ = 1.61 g cm$^{-3}$, $Z$ = 4.

## Introduction

Metal complexes with acetylacetonato and substituted acetylacetonato ligands have been frequently employed in the synthesis of ceramic materials by chemical processes due to their high solubility and volatility.[1] Fluorinated acetylacetonato ligands have been known to further enhance the solubility and volatility of the metal complexes in comparison with the corresponding unfluorinated ligands, and thus they have been widely used in the synthesis of various mononuclear and polynuclear metal complexes.[1,2] However, despite their potential applications, the reactivity and stability of metal complexes with fluorinated acetylacetonato ligands have not been well examined. We have been investigating the syntheses of Ln − Cu complexes by using Ln(hfacac)$_3$ (Ln = Y, Nd, Pr) and Cu-

(OCH$_3$)$_2$ or Cu$_2$(O$_2$CCH$_3$)$_4$(H$_2$O$_2$)$_2$ as the starting material and the bdmap ligand as the bridging ligand, where hfacac = hexafluoroacetylacetonato and bdmap = 1,3-bis(dimethylamino)-2-propanolato. During our investigation we have found that although the mixed metal complexes could be obtained, the hfacac ligand in this system displays a complicated reactivity pattern affected by the presence of Lewis bases, metal ions, and moisture.[3] In this report, the reactions of Ln(hfacac)$_3$ (Ln = Y, Pr, Nd) with bdmapH, Cu(OCH$_3$)$_2$ and Cu$_2$(O$_2$CCH$_3$)$_4$-(H$_2$O)$_2$ are described. The structures, thermal behaviors, and magnetic properties of three new lanthanides (yttrium) and copper complexes Ln$_2$(hfacac)$_4$(bdmap)$_2$(H$_2$O)$_2$(THF)$_2$ (**1**), LnCu-(bdmapH)$_2$(hfacac)$_2$(O$_2$CCF$_3$)L (**2**), L = 2-methyl-2,4,6-tris-(trifluoromethyl)-1,3-dioxane-4,6-diolato, and LnCu$_2$(hfacac)-(bdmap)$_3$(O$_2$CCH$_3$)$_2$(O$_2$CCF$_3$)(hfacacH) (**3**) are presented.

## Experimental Section

All reactions were carried out by using the standard Schlenk vacuum line techniques under a nitrogen atmosphere. Ln(hfacac)$_3$ was purchased from Strem Chemicals, Inc. 1,3-bis(dimethylamino)-2-propanol was obtained from Spectrum Chemical Mfg. Corp. Cu(OCH$_3$)$_2$, hexafluoroacetylacetone, and 1,1,1-trifluoroacetone were purchased from Aldrich Chemical Co. Solvents were distilled prior to use. Elemental analyses were performed at Guelph Chemical Laboratories Ltd, Guelph, Ontario, and Desert Analytics, Tucson, AZ. Thermal analyses were performed on a Perkin Elmer TGA-7 analyzer under an oxygen atmosphere. EPR spectra were recorded on a Bruker ESP 300E spectrometer. IR spectra were taken on a Nicolet FTIR-5DX spectrometer.

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**Reaction of Pr(hfacac)₃ with bdmapH and Cu(OCH₃)₂.** A solution of Cu(OCH₃)₂ (33 mg, 0.26 mmol) and bdmapH (77 mg, 0.53 mmol) in 20 mL of THF was stirred for 1 h at 23 °C. To this solution was added Pr(hfacac)₃ (200 mg, 0.26 mmol). The mixture was stirred for an additional 3 h. A clear blue-green solution was obtained. After the volume of the solution was reduced to about 3 mL, excess hexane was added. The solution was kept at 0 °C for a few days, and yellow-green crystals of Pr₂(hfacac)₄(bdmap)₂(H₂O)₂(THF)₂ (1) were obtained (about 30% yield). The mother liquid was concentrated further and additional amount of hexane was added. Blue crystals of PrCu-(bdmapH)₂(hfacac)₂(O₂CCF₃)L (2a) along with a blue oily material formed. After repeated washing and recrystallization from THF and hexane, crystals of 2a were isolated in about 15% yield. Mp for compound 1: 175 °C. IR (1, KBr, cm⁻¹): 1109 m, 1141 vs, 1192 s, 1201 s, 1471 m, 1499 s, 1527 m, 1558 m, 1655 s. Anal. Calcd for the vacuum-dried sample of 1, C₃₄H₄₂O₁₂Pr₂F₂₄N₄: C, 28.43; H, 2.95; N, 3.90. Found: C, 29.52; H, 3.60; N, 3.59. We believe that the high carbon and hydrogen content in the sample was caused by the incomplete removal of the THF solvent molecule from the sample. Mp for compound 2a: 170 °C. Anal. Calcd for 2a, C₃₄H₄₃PrCuF₂₄O₁₂N₄: C, 30.03; H, 3.19; N, 4.12. Found: C, 30.89; H, 3.09; N, 4.12.

Compound **2b**, YCu(bdmapH)₂(hfacac)₂(O₂CCF₃)L, was obtained in 17% yield from the reaction of Y(hfacac)₃ with bdmapH and Cu(OCH₃)₂ by a similar procedure. Mp for **2b**: 160 °C. IR (KBr, cm⁻¹): 1140 vs, 1201 s, 1261 s, 1469 m, 1532 s, 1673 s. Anal. Calcd for C₃₄H₄₃YCuF₂₄O₁₂N₄: C, 31.21; H, 3.31; N, 4.28. Found: C, 31.25; H, 3.14; N, 4.29.

**Synthesis of Pr₂(hfacac)₄(bdmap)₂(H₂O)₂(THF)₂ (1).** Compound **1** can be obtained in 44% yield (50 mg, 0.032 mmol) from the reaction of Pr(hfacac)₃ (110 mg, 0.14 mmol) with bdmapH (25 mg, 0.17 mmol) and H₂O (3 mg, 0.17 mmol) in 4 mL of THF at 23 °C and by subsequent crystallization from a THF/hexane solution. Attempts to synthesize the analogous yttrium compound were unsuccessful.

**Synthesis of PrCu(bdmapH)₂(hfacac)₂(O₂CCF₃)L (2a).** Cu-(OCH₃)₂ (34 mg, 0.27 mmol) and bdmapH (80 mg, 0.55 mmol) were mixed in 15 mL of THF at 23 °C. HO₂CCF₃ (32 mg, 0.28 mmol) was then added. A blue-green solution was obtained. After about 10 min of stirring, Pr(hfacac)₃ (200 mg, 0.26 mmol) was added. The solution became light green-blue. 1,1,1-Trifluoroacetone (30 mg, 0.27 mmol) and H₂O (5 mg, 0.28 mmol) were added. This mixture was stirred at 23 °C for 2 h. A royal blue solution was obtained. The solution was concentrated to about 4 mL *in vacuo*, and excess hexane was added. The colorless solid was removed by filtration. The filtrate was further concentrated, and an additional amount of hexane was added. After the solution was allowed to stand at 23 °C for several days, dark blue crystals of 2a were obtained (100 mg, 0.074 mmol, 28% yield). Further concentrating the mother liquid resulted in not only the formation of more crystals of compound 2a but also the formation of a blue oil, which made it difficult to isolate additional crystals of compound 2a. The high solubility of 2a and the formation of oil are believed to be responsible for the low isolated yield of compound 2a from this reaction. Compound 2b was also obtained by the same procedure.

**Synthesis of PrCu₂(hfacac)(bdmap)₃(O₂CCH₃)₂(O₂CCF₃)(hfacacH)-(THF) (3b).** Cu₂(O₂CCH₃)₄(H₂O)₂ (363 mg, 0.91 mmol) and bdmapH (400 mg, 2.74 mmol) were mixed in 30 mL of THF at 23 °C. After a few minutes, Pr(hfacac)₃ (748 mg, 0.98 mmol) was added. This mixture was stirred for an additional 10 min. The resulting blue solution was allowed to stand at 23 °C for a few hours. The white-blue solid precipitated was removed by filtration. The solution was concentrated to about 7 mL *in vacuo*. Excess diethyl ether was then added to this solution to crystallize the product. After a few days, blue crystals of 3b were obtained (602 mg, 0.42 mmol, yield 46%, based on copper). Mp: 105–110 °C. Anal. Calcd for C₃₂H₅₈PrCu₂F₉O₁₁N₆·(hfacacH)-(THF): C, 34.63; H, 4.79; N, 5.91. Found: C, 34.40; H, 4.83; N, 6.13.

Compound **3a**, NdCu₂(hfacac)(bdmap)₃(O₂CCH₃)₂(O₂CCF₃)(hfacacH)-(THF), was obtained in 48% yield by the similar procedure described above. Mp: 110 °C. IR (KBr, cm⁻¹): 1096 w, 1141 vs, 1199 s, 1253 s, 1433 m, 1464 m, 1502 w, 1560 s, 1667 s. Anal. Calcd for C₃₂H₅₈NdCu₂F₉O₁₁N₆·hfacacH·THF: C, 34.55; H, 4.77; N, 5.90. Found: C, 34.96; H, 5.10; N, 5.92.

**Attempted Synthesis of the 2-Methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diol Ligand.** A 280 mg (2.15 mmol) sample of

tetramethylpropanediamine (tmpda), 200 mg (1.78 mmol) of 1,1,1-trifluoroacetone, and 40 mg (2.20 mmol) of H₂O were mixed in diethyl ether at 23 °C. A 450 mg (2.20 mmol) sample of hexafluoroacetyl-acetone was then added to the solution. A clear colorless solution was obtained and kept at 23 °C for about 12 h. The crystals of [tmpdaH₂][O₂CCF₃]₂ precipitated from the solution in nearly quantitative yield.

**Magnetic Susceptibility Measurements.** The magnetic susceptibilities at 0.49 kG in the temperature range 5–300 K for 1 and 3b were measured on a SQUID device (SHE variable-temperature susceptometer) at Michigan State University. The samples were quenched to 5 K at zero field. The field was cycled to minimize the residual field. The samples were loaded into a nitrogen-filled glovebag and run in an Al–Si alloy bucket.

**X-ray Diffraction Analysis.** Light yellow-green crystals of 1 and blue crystals of 2a and 2b were obtained from THF/hexane solutions by slow diffusion of solvents. The blue crystals of 3a and 3b were obtained from the THF/diethyl ether solution. These crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV and 35 mA over the range 3 < 2θ < 50° for 1 and 2a, 3 < 2θ < 48° for 3a. Cell constants and the orientation matrix for data collection of 1 were obtained from 20 reflections in the range 13 < 2θ < 24°. The initial orientation matrix for 2a was obtained from 20 reflections (8 < 2θ < 12°) which was further refined by using 18 high angle reflections (20 < 2θ < 26°). The cell constants and the orientation matrix for 3a were obtained from 20 reflections (10 < 2θ < 14°). Three standard reflections were measured every 147 reflections. Data were processed on a VAX workstation 3520 using the TEXSAN crystallographic package (version 5.0). Data were corrected for Lorentz–polarization effects. Empirical absorption corrections were applied for all crystals.

The crystals of 1 belong to the triclinic space group PT̄. The crystals of 2a and 2b are isomorphous. Structural solution and refinements were carried out for 2a only. The compound 2a crystallizes in the monoclinic crystal system. The systematic absences agree with two possible space groups Cc and C2/c. The acentric space group Cc was chosen. The correctness of this choice was confirmed by the successful solution and refinement of the structure. The monoclinic space group P2₁/n for 3a was uniquely determined by the systematic absences. The positions of metal atoms in all structures were determined by the direct methods (MITHRIL). Other non-hydrogen atoms were located by subsequent difference Fourier syntheses. Three of the four CF₃ groups in 1 have a C₂ rotation disorder. Two sets of fluorine atoms for each of the disordered CF₃ groups were located and refined successfully with a 50% occupancy factor. Two of the carbon atoms of the THF molecule in 1 are disordered over two sites. The carbon atoms on the disordered sites were refined with a 50% occupancy factor. All CF₃ groups in 2a displayed some degree of disorders and were refined as rigid groups with the fixed C–F bond length of 1.31 Å and F–C–F angle of 109°. Two sets of fluorine atoms for C(3), C(7), and C(8) in 2a were located and refined with 50% occupancy factors, respectively. The trifluoromethyl group bonded to C(18) in 2a was disordered over both the axial and equatorial positions. Two sets of fluorine atoms were located and refined with a 50% occupancy factor for both positions. Compound 3a also displayed significant disorder. One of the CF₃ groups on the hfacac ligand showed a C₂ disorder. Two sets of fluorine atoms bonded to the C(26) atom in 3a were located and refined successfully with a 50% occupancy factor. There is a free hexafluoroacetylacetone (hfacacH) molecule in the crystal lattice of 3a. One of the CF₃ groups of the hfacacH also showed a C₂ disorder. Six fluorine atoms for this disordered CF₃ groups were located and refined successfully with a 50% occupancy factor. A disordered THF solvent molecule was also located in the lattice of 3a. It appeared that the oxygen atom of the THF molecule was disordered over two sites related by a C₂ rotation. However, the refinement of the disordered THF was not satisfactory as indicated by the large thermal parameters of atoms in this group. All non-hydrogen atoms except the disordered THF molecule in 1 were refined anisotropically. Due to the limited data, only metal atoms and some of the oxygen atoms in 2a were refined anisotropically. Metal atoms, nondisordered fluorine atoms, and some of the oxygen atoms in 3a were refined anisotropically. Hydrogen atoms except those of the disordered THF

**Table 1.** Crystallographic Data

|  | 1 | 2a | 3a |
|---|---|---|---|
| formula | $C_{42}H_{58}Pr_2F_{24}O_{16}N_4$ | $C_{34}H_{43}PrCuF_{24}$-$O_{12}N_4$ | $C_{37}H_{60}NdCu_2F_{15}$-$O_{13}N_6$·THF |
| fw | 1580.7 | 1360.2 | 1425.3 |
| space group | $P\overline{1}$ | $Cc$ | $P2_1/n$ |
| $a$, Å | 12.00(1) | 18.205(5) | 12.027(4) |
| $b$, Å | 13.71(1) | 18.350(6) | 15.222(4) |
| $c$, Å | 11.284(7) | 15.924(4) | 32.70(2) |
| $\alpha$, deg | 112.59(6) | | |
| $\beta$, deg | 107.06(7) | 94.96(2) | 100.13(4) |
| $\gamma$, deg | 97.48(8) | | |
| $V$, Å$^3$ | 1575(3) | 5299(2) | 5894(5) |
| $Z$ | 1 | 4 | 4 |
| $d_{calc}$, gcm$^{-3}$ | 1.57 | 1.72 | 1.61 |
| $\mu$ (Mo, K$\alpha$), cm$^{-1}$ | 16.47 | 14.46 | 16.93 |
| $R^a$ | 0.047 | 0.066 | 0.090 |
| $R_w{}^b$ | 0.053 | 0.046 | 0.102 |

$^a R = \sum_{i=1}^n (|F_{obs}|_i - |F_{obs}|_i/\sum_{i=1}^n |F_{obs}|_i)$. $^b R_w = (\sum_{i=1}^n W_i(|F_{obs}|_i - |F_{calc}|_i)^2/\sum_{i=1}^n W_i|F_{obs}|_i^2)^{1/2}$, $W = 1/\sigma^2(F_{obs})$.

molecules in **1a** and **3a** were calculated. The positions of hydrogen atoms except those on the methyl group bonded to C(18) in **2a** were calculated. Their temperature factors were tied to the temperature factor of the carbon atoms to which they are bonded (multiplied by 1.10). Their contribution in structural factor calculations was included. The unit cell parameters for **2b** and **3b** are nearly identical to the corresponding ones of **2a** and **3a**. The structural characterizations for both compound were, therefore, not performed. The data for the X-ray diffraction analysis are given in Table 1.

## Results and Discussion

**Synthesis and Structure of Pr$_2$(hfacac)$_4$(bdmap)$_2$(H$_2$O)$_2$-(THF)$_2$ (1).** Compound **1** was initially obtained from the reaction of Pr(hfacac)$_3$ with Cu(OMe)$_2$ and bdmapH in a 1:1:2 ratio in THF. This compound can also be obtained readily in 40% yield by the independent synthesis where Pr(hfacac)$_3$ was reacted with bdmapH and H$_2$O in a 1:1:1 ratio in THF (eq 1

$$2Pr(hfacac)_3 + 2bdmapH + 2H_2O \rightarrow$$
$$Pr_2(hfacac)_4(bdmap)_2(H_2O)_2(THF)_2 + 2hfacacH \quad (1)$$
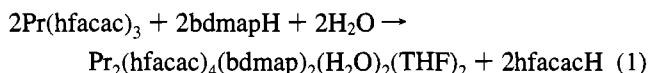
and Scheme 1). The crystal structure of **1** has been determined by X-ray diffraction analysis. Important atomic positional and

thermal parameters are given in Table 2a. Selected bond distances and angles are given in Table 3a. An ORTEP diagram showing the molecular structure of **1** is given in Figure 1. The molecule of **1** has an inversion center. The two Pr(III) centers are bridged by two oxygen atoms of the bdmap ligands with the Pr–Pr' separation being 3.951(4) Å. Each Pr(III) center is also coordinated by four oxygen atoms of the hfacac ligands, two nitrogen atoms of the bdmap ligands, and a H$_2$O molecule. The Pr–O distances range from 2.337(5) to 2.563(6) Å while the Pr–N distances are significantly longer, 2.801(6) and 2.826(6) Å. The similar situation has been observed in the previously reported compound[4] LaCu$_2$(bdmap)$_3$(O$_2$CCF$_3$)$_4$. We believe that the long Ln–N bond length is due to the relative poor affinity of the amino nitrogen to the lanthanide center, in comparison with the oxygen atom. The disordered THF solvent molecule is hydrogen-bonded to the H$_2$O ligand as evidenced by the O(6)–O(7) distance of 2.68(2) Å. A dozen of dinuclear lanthanide (yttrium) complexes with alkoxy bridges have been reported previously.[5] Compound **1** is one of the few dinuclear lanthanide complexes where aminoalkoxy ligands function as the bridging ligand. The facile formation of **1** is probably due to the fact that Ln(hfacac)$_3$ complexes have the tendency to form adducts with donor ligands so that the coordination saturation on the metal center can be achieved.[6]

**Synthesis and Structure of LnCu(bdmapH)$_2$(hfacac)$_2$(O$_2$-CCF$_3$)L (Ln = Pr, 2a; Ln = Y, 2b).** The Ln$^{III}$–Cu$^{II}$ (Ln = Y, Pr) dinuclear complex **2** was initially isolated as a blue crystalline product in low yield along with compound **1** (Ln = Pr) from the reaction of Cu(OMe)$_2$, Ln(hfacac)$_3$, and bdmapH in a 1:1:2 ratio in THF at 23 °C, attempted for the synthesis of the LnCu(bdmap)$_2$(hfacac)$_3$ compound (Scheme 1). Single-crystal X-ray diffraction and elemental analyses unambiguously established that compound **2** has the formula Ln$^{III}$Cu$^{II}$-(bdmapH)$_2$(hfacac)$_2$(O$_2$CCF$_3$)L (Ln = Pr, **2a**; Ln = Y, **2b**; L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato). Compounds **2a** and **2b** have the same structures in the solid state. Although discrete dinuclear Ln$^{III}$–Cu$^{II}$ complexes are rare, a few examples have been reported previously.[10] Selected atomic positional and thermal parameters for **2a** are listed in Table 2b. Important bond lengths and angles are given in Table 3b. The structure of **2a** is shown in Figure 2. A side view of
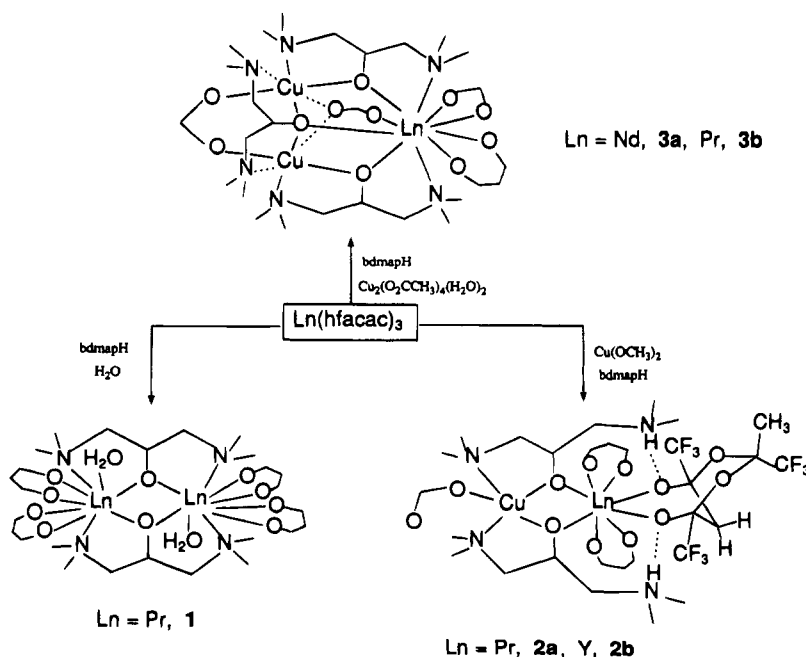
**Scheme 1**



Ln = Nd, **3a**, Pr, **3b**

Ln = Pr, **1**

Ln = Pr, **2a**, Y, **2b**

**Table 2.** Selected Atomic Coordinates and Thermal Parameters $(B_{eq})^a$

| atom | $x$ | $y$ | $z$ | $B(eq)$, Å² | atom | $x$ | $y$ | $z$ | $B(eq)$, Å² |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | |

(a) Compound **1**

| atom | $x$ | $y$ | $z$ | $B(eq)$, Å² | atom | $x$ | $y$ | $z$ | $B(eq)$, Å² |
|---|---|---|---|---|---|---|---|---|---|
| Pr | 0.08480(4) | 0.15216(3) | 0.14411(4) | 3.25(1) | C(5) | 0.080(1) | 0.2538(9) | −0.110(1) | 7.0(4) |
| O(1) | 0.0615(4) | 0.0165(4) | −0.0720(4) | 3.7(1) | C(6) | 0.123(1) | −0.2628(8) | −0.309(1) | 7.3(4) |
| O(2) | 0.1665(5) | 0.0604(5) | 0.2972(5) | 5.1(2) | C(7) | −0.000(1) | −0.1900(9) | −0.440(1) | 7.2(4) |
| O(3) | 0.3034(5) | 0.1437(5) | 0.1827(6) | 5.6(2) | C(8) | 0.2673(8) | 0.0593(7) | 0.3684(8) | 4.8(3) |
| O(4) | 0.2315(6) | 0.2945(5) | 0.3817(6) | 6.3(2) | C(9) | 0.3789(7) | 0.0921(8) | 0.363(1) | 5.7(3) |
| O(5) | 0.0669(5) | 0.3439(4) | 0.1992(5) | 5.2(2) | C(10) | 0.3865(7) | 0.1275(8) | 0.265(1) | 5.3(3) |
| O(6) | −0.1168(6) | 0.1502(5) | −0.0187(6) | 6.7(2) | C(11) | 0.266(1) | 0.014(1) | 0.473(1) | 7.9(6) |
| N(1) | 0.1753(7) | 0.2293(5) | −0.0153(7) | 5.0(2) | C(12) | 0.512(1) | 0.155(2) | 0.258(2) | 8.7(7) |
| N(2) | 0.0666(6) | −0.1742(5) | −0.2978(7) | 4.9(2) | C(13) | 0.120(1) | 0.4416(7) | 0.296(1) | 5.6(3) |
| C(1) | 0.2123(8) | 0.1350(7) | −0.0976(8) | 5.0(3) | C(14) | 0.209(1) | 0.4725(8) | 0.420(1) | 7.3(4) |
| C(2) | 0.1126(7) | 0.0288(6) | −0.1664(7) | 4.0(2) | C(15) | 0.260(1) | 0.3940(8) | 0.454(1) | 6.6(4) |
| C(3) | 0.1609(7) | −0.0696(7) | −0.2224(8) | 4.8(3) | C(16) | 0.071(1) | 0.5299(9) | 0.270(1) | 8.1(5) |
| C(4) | 0.282(1) | 0.3252(7) | 0.067(1) | 6.5(4) | C(17) | 0.360(3) | 0.434(2) | 0.592(2) | 14(1) |

(b) Compound **2a**

| atom | $x$ | $y$ | $z$ | $B(eq)$, Å² | atom | $x$ | $y$ | $z$ | $B(eq)$, Å² |
|---|---|---|---|---|---|---|---|---|---|
| Pr | 0.0245 | 0.75752(6) | 0.2919 | 3.20(4) | C(9) | −0.004(2) | 0.835(1) | 0.488(2) | 6.4(7) |
| Cu | −0.0916(2) | 0.6152(1) | 0.2801(2) | 4.0(1) | C(10) | −0.081(2) | 0.861(2) | 0.465(2) | 10(1) |
| O(1) | −0.064(1) | 0.500(1) | 0.253(1) | 8(1) | C(12) | −0.2019(8) | 0.866(1) | 0.374(1) | 10.6(9) |
| O(2) | 0.000(2) | 0.476(2) | 0.138(2) | 18(3) | C(11) | −0.118(2) | 0.844(2) | 0.387(3) | 12(1) |
| O(3) | −0.0061(7) | 0.6445(7) | 0.3546(8) | 3.7(7) | C(13) | 0.253(2) | 0.790(1) | 0.413(2) | 7.5(8) |
| O(4) | −0.0416(8) | 0.6725(7) | 0.2006(8) | 3.6(7) | C(14) | 0.210(1) | 0.754(1) | 0.328(1) | 4.9(5) |
| O(5) | −0.043(1) | 0.8361(8) | 0.176(1) | 5(1) | C(15) | 0.198(1) | 0.811(1) | 0.266(1) | 3.4(4) |
| O(6) | 0.0459(8) | 0.8888(8) | 0.3202(9) | 5.1(4) | C(16) | 0.170(1) | 0.786(1) | 0.177(1) | 4.3(5) |
| O(7) | −0.1010(9) | 0.7946(9) | 0.332(1) | 5.5(4) | C(17) | 0.178(2) | 0.846(2) | 0.115(2) | 7.4(8) |
| O(8) | 0.0272(8) | 0.7843(8) | 0.4514(9) | 4.5(3) | C(18) | 0.254(2) | 0.671(2) | 0.211(2) | 9.3(9) |
| O(9) | 0.1448(8) | 0.7216(7) | 0.3522(9) | 4.7(3) | C(19) | 0.335(2) | 0.633(2) | 0.187(2) | 12(1) |
| O(10) | 0.1021(7) | 0.7582(8) | 0.1729(8) | 4.5(3) | C(20) | 0.196(3) | 0.612(3) | 0.216(3) | 13(1) |
| O(11) | 0.264(1) | 0.697(1) | 0.303(1) | 9.5(6) | C(21) | −0.068(1) | 0.556(1) | 0.443(2) | 5.7(6) |
| O(12) | 0.224(1) | 0.732(1) | 0.147(1) | 10.0(6) | C(22) | −0.004(1) | 0.613(1) | 0.443(1) | 4.5(5) |
| N(1) | −0.135(1) | 0.585(1) | 0.393(1) | 5.9(5) | C(23) | 0.068(1) | 0.569(1) | 0.452(2) | 6.2(6) |
| N(2) | 0.137(1) | 0.611(1) | 0.467(1) | 5.3(5) | C(24) | −0.166(2) | 0.652(2) | 0.429(2) | 9(1) |
| N(3) | −0.181(1) | 0.618(1) | 0.188(1) | 4.4(4) | C(25) | −0.190(2) | 0.527(2) | 0.392(2) | 9.4(9) |
| N(4) | 0.033(1) | 0.703(1) | 0.030(1) | 4.9(4) | C(26) | 0.136(2) | 0.652(2) | 0.551(2) | 8.3(8) |
| C(1) | −0.029(2) | 0.464(2) | 0.207(3) | 9(1) | C(27) | 0.194(2) | 0.566(2) | 0.458(2) | 7.6(8) |
| C(2) | −0.018(1) | 0.389(1) | 0.232(2) | 28(1) | C(28) | −0.140(1) | 0.618(2) | 0.114(2) | 6.5(7) |
| C(3) | −0.122(1) | 0.918(1) | 0.089(2) | 10(1) | C(29) | −0.078(1) | 0.671(1) | 0.118(1) | 4.2(5) |
| C(4) | −0.065(2) | 0.900(2) | 0.175(2) | 6.3(7) | C(30) | −0.020(2) | 0.647(1) | 0.054(2) | 6.4(6) |
| C(5) | −0.032(2) | 0.955(2) | 0.231(2) | 7.7(8) | C(31) | −0.219(2) | 0.681(2) | 0.193(2) | 9(1) |
| C(6) | 0.020(2) | 0.947(1) | 0.304(2) | 6.3(6) | C(32) | −0.229(2) | −0.557(2) | 0.182(2) | 8.9(8) |
| C(7) | 0.054(1) | 1.018(1) | 0.347(2) | 6.0(6) | C(33) | −0.004(1) | 0.762(2) | −0.020(2) | 6.9(7) |
| C(8) | 0.036(2) | 0.852(2) | 0.579(2) | 8.9(9) | C(34) | 0.087(2) | 0.670(2) | −0.015(2) | 9(1) |

(c) Compound **3a**

| atom | $x$ | $y$ | $z$ | $B(eq)$, Å² | atom | $x$ | $y$ | $z$ | $B(eq)$, Å² |
|---|---|---|---|---|---|---|---|---|---|
| Nd | 0.4709(1) | 0.8302(1) | 0.12571(4) | 3.12(6) | C(7) | 0.726(2) | 0.968(2) | 0.145(1) | 6.9(8) |
| Cu(1) | 0.5523(3) | 0.6092(2) | 0.1440(1) | 3.7(1) | C(8) | 0.245(2) | 0.727(2) | −0.0012(8) | 5.4(7) |
| Cu(2) | 0.3484(3) | 0.6435(2) | 0.0705(1) | 4.2(2) | C(9) | 0.318(2) | 0.798(2) | 0.0252(7) | 4.1(6) |
| O(1) | 0.603(1) | 0.7263(9) | 0.1586(4) | 2.5(3) | C(10) | 0.246(2) | 0.884(2) | 0.0220(8) | 5.4(7) |
| O(2) | 0.343(1) | 0.769(1) | 0.0664(5) | 3.7(3) | C(11) | 0.203(3) | 0.575(2) | −0.005(1) | 9(1) |
| O(3) | 0.400(1) | 0.659(1) | 0.1308(4) | 3.4(7) | C(12) | 0.384(3) | 0.622(2) | −0.015(1) | 7.5(8) |
| O(4) | 0.430(1) | 0.839(1) | 0.1987(5) | 4.5(4) | C(13) | 0.161(3) | 1.008(2) | −0.013(1) | 8.3(9) |
| O(5) | 0.269(1) | 0.881(1) | 0.1265(5) | 5.0(9) | C(14) | 0.354(3) | 0.972(2) | −0.021(1) | 7.1(8) |
| O(6) | 0.466(1) | 0.992(1) | 0.1466(5) | 4.4(4) | C(15) | 0.206(2) | 0.657(2) | 0.1405(8) | 5.5(6) |
| O(7) | 0.465(1) | 0.963(1) | 0.0808(6) | 5(1) | C(16) | 0.326(2) | 0.618(2) | 0.1531(7) | 3.3(5) |
| O(8) | 0.594(1) | 0.804(1) | 0.0731(4) | 4.0(8) | C(17) | 0.371(2) | 0.628(1) | 0.1989(7) | 3.2(5) |
| O(9) | 0.568(1) | 0.659(1) | 0.0663(5) | 4.8(9) | C(18) | 0.105(3) | 0.543(2) | 0.096(1) | 8(1) |
| O(10) | 0.366(1) | 0.515(1) | 0.0715(5) | 5.2(9) | C(19) | 0.067(3) | 0.696(2) | 0.084(1) | 8.1(9) |
| O(11) | 0.510(1) | 0.490(1) | 0.1252(6) | 6(1) | C(20) | 0.467(2) | 0.494(2) | 0.2223(9) | 6.5(7) |
| N(1) | 0.720(2) | 0.574(1) | 0.1530(6) | 4.2(4) | C(21) | 0.542(3) | 0.628(2) | 0.248(1) | 6.9(8) |
| N(2) | 0.686(2) | 0.892(1) | 0.1639(6) | 4.2(5) | C(22) | 0.398(3) | 0.893(2) | 0.262(1) | 5.6(7) |
| N(3) | 0.296(2) | 0.639(1) | 0.0084(6) | 5.1(5) | C(23) | 0.361(2) | 0.883(2) | 0.2136(7) | 3.8(5) |
| N(4) | 0.243(2) | 0.936(1) | −0.0166(6) | 4.1(5) | C(24) | 0.263(2) | 0.925(2) | 0.1962(8) | 4.7(6) |
| N(5) | 0.155(2) | 0.632(2) | 0.0988(7) | 6.0(6) | C(25) | 0.224(2) | 0.917(2) | 0.1544(8) | 4.0(5) |
| N(6) | 0.478(2) | 0.586(1) | 0.2109(6) | 4.8(5) | C(26) | 0.102(4) | 0.962(3) | 0.136(1) | 9(1) |
| C(1) | 0.781(2) | 0.656(2) | 0.1530(8) | 5.2(6) | C(27) | 0.461(2) | 1.017(2) | 0.1089(9) | 4.6(6) |
| C(2) | 0.720(2) | 0.731(1) | 0.1700(7) | 3.0(5) | C(28) | 0.445(2) | 1.113(2) | 0.099(1) | 6.7(8) |
| C(3) | 0.764(2) | 0.820(2) | 0.1605(8) | 5.3(6) | C(29) | 0.611(2) | 0.729(2) | 0.0600(8) | 3.7(5) |
| C(4) | 0.748(2) | 0.516(2) | 0.1214(9) | 5.6(7) | C(30) | 0.691(3) | 0.729(2) | 0.029(1) | 4.9(6) |
| C(5) | 0.749(2) | 0.528(2) | 0.193(1) | 6.2(7) | C(31) | 0.433(2) | 0.470(2) | 0.0986(8) | 3.3(5) |
| C(6) | 0.683(2) | 0.911(2) | 0.2072(9) | 5.3(7) | C(32) | 0.412(2) | 0.370(2) | 0.092(1) | 6.6(8) |

$^a B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha).$

this compound showing the coordination geometry of the Cu-(II) and the Pr(III) centers is given in Figure 3. The Cu(II) and Pr(III) ions are bridged by two oxygen atoms from the two bdmapH ligands with a separation distance of 3.355(3) Å.

Similar Cu−Ln separations have been observed previously.[1a,6a,4,7] The Cu(II) center is coordinated by two additional nitrogen atoms with normal Cu−N bond lengths. The fifth position of the Cu(II) center is occupied by an oxygen atom of a trifluo-

**Table 3.** Selected Bond Lengths (Å) and Angles (deg)

### (a) Compound 1
#### Bond Lengths

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pr−O(1) | 2.337(5) | Pr−O(1)′ | 2.399(5) | N(1)−C(5) | 1.49(1) | N(2)−C(3) | 1.46(1) |
| Pr−O(2) | 2.555(5) | Pr−O(3) | 2.556(6) | N(2)−C(6) | 1.44(1) | N(2)−C(7) | 1.48(1) |
| Pr−O(4) | 2.532(6) | Pr−O(5) | 2.513(6) | C(1)−C(2) | 1.51(1) | C(2)−C(3) | 1.52(1) |
| Pr−O(6) | 2.563(6) | Pr−N(1) | 2.801(6) | C(8)−C(9) | 1.38(1) | C(8)−C(11) | 1.53(1) |
| Pr−N(2) | 2.826(6) | O(1)−C(2) | 1.426(7) | C(9)−C(10) | 1.39(1) | C(10)−C(12) | 1.54(1) |
| O(2)−C(8) | 1.247(9) | O(3)−C(10) | 1.254(9) | C(13)−C(14) | 1.35(1) | C(13)−C(16) | 1.50(1) |
| O(4)−C(15) | 1.23(1) | O(5)−C(13) | 1.28(1) | C(14)−C(15) | 1.43(1) | C(15)−C(17) | 1.49(2) |
| N(1)−C(1) | 1.48(1) | N(1)−C(4) | 1.47(1) | | | | |

#### Bond Angles

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(2)−Pr−O(5) | 132.4(2) | O(2)−Pr−O(6) | 140.1(2) | N(1)−Pr−N(2) | 146.1(2) | O(1)−Pr−O(4)′ | 131.4(2) |
| O(2)−Pr−N(1) | 133.6(2) | O(2)−Pr−N(2) | 77.5(2) | O(1)−Pr−O(5)′ | 132.0(2) | O(1)−Pr−O(6)′ | 71.9(2) |
| O(3)−Pr−O(4) | 68.0(2) | O(3)−Pr−O(5) | 111.6(2) | O(1)−Pr−N(1) | 129.3(2) | O(1)−Pr−N(2) | 66.6(2) |
| O(3)−Pr−O(6) | 147.5(2) | O(3)−Pr−N(1) | 68.8(2) | O(2)−Pr−O(3) | 65.1(2) | O(2)−Pr−O(4) | 69.4(2) |
| O(3)−Pr−N(2) | 136.6(2) | O(1)−Pr−O(1)′ | 66.9(2) | Pr−O(1)−Pr′ | 113.1(2) | C(1)−N1−C(4) | 108.7(7 |
| O(4)−Pr−O(5) | 66.4(2) | O(1)−Pr−O(2) | 100.2(2) | C(1)−N(1)−C(5) | 109.8(7) | C(4)−N1−C(5) | 109.9(7) |
| O(4)−Pr−O(6) | 132.2(2) | O(1)−Pr−O(3) | 78.8(2) | C(3)−N(2)−C(6) | 109.2(7) | C(3)−N2−C(7) | 109.3(7) |
| O(4)−Pr−N(1) | 98.4(2) | O(1)−Pr−O(4) | 146.6(2) | C(6)−N(2)−C(7) | 107.6(7) | N(1)−C(1)−C(2) | 111.6(6) |
| O(4)−Pr−N(2) | 79.1(2) | O(1)−Pr−O(5) | 126.5(2) | O(1)−C(2)−C(1) | 111.4(6) | O(1)−C(2)−C(3) | 108.3(6) |
| O(5)−Pr−O(6) | 68.9(2) | O(1)−Pr−O(6) | 76.5(2) | C(1)−C(2)−C(3) | 110.7(6) | N(2)−C(3)−C(2) | 113.0(6) |
| O(5)−Pr−N(1) | 70.6(2) | O(1)−Pr−N(1) | 65.1(2) | O(2)−C(8)−C(9) | 128.1(7) | O(2)−C(8)−C(11) | 115.3(8) |
| O(5)−Pr−N(2) | 77.7(2) | O(1)−Pr−N(2) | 131.1(2) | C(9)−C(8)−C(11) | 116.6(8) | C(8)−C(9)−C(10) | 119.9(7) |
| O(6)−Pr−N(1) | 81.8(2) | O(1)−Pr−O(2)′ | 70.4(2) | O(3)−C(10)−C(9) | 127.8(8) | O(3)−C(10)−C(12) | 115.3(9) |
| O(6)−Pr−N(2) | 75.8(2) | O(1)−Pr−O(3)′ | 116.4(2) | C(9)−C(10)−C(12) | 116.9(9) | | |

### (b) Compound 2a
#### Bond Lengths

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pr−Cu | 3.355(3) | O(12)−C(16) | 1.50(2) | O(1)−C(1) | 1.19(4) | C(3)−C(4) | 1.66(4) |
| Pr−O(3) | 2.39(1) | O(12)−C(18) | 1.58(4) | O(2)−C(1) | 1.28(4) | C(4)−C(5) | 1.44(4) |
| Pr−O(4) | 2.39(1) | N(1)−C(21) | 1.50(3) | O(3)−C(22) | 1.38(2) | C(5)−C(6) | 1.44(4) |
| Pr−O(5) | 2.57(2) | N(1)−C(24) | 1.49(4) | O(4)−C(29) | 1.43(2) | C(6)−C(7) | 1.57(3) |
| Pr−O(6) | 2.47(1) | N(1)−C(25) | 1.45(3) | O(5)−C(4) | 1.25(3) | C(8)−C(9) | 1.60(4) |
| Pr−O(7) | 2.52(2) | N(2)−C(23) | 1.49(3) | O(6)−C(6) | 1.19(2) | C(9)−C(10) | 1.49(4) |
| Pr−O(8) | 2.58(1) | N(2)−C(26) | 1.53(3) | O(7)−C(11) | 1.30(4) | C(10)−C(11) | 1.40(5) |
| Pr−O(9) | 2.41(1) | N(2)−C(27) | 1.35(3) | O(8)−C(9) | 1.26(3) | C(13)−C(14) | 1.64(3) |
| Pr−O(10) | 2.46(1) | N(3)−C(28) | 1.44(3) | O(9)−C(14) | 1.41(2) | C(14)−C(15) | 1.44(3) |
| Cu−O(1) | 2.23(2) | N(3)−C(31) | 1.35(3) | O(10)−C(16) | 1.33(2) | C(15)−C(16) | 1.53(3) |
| Cu−O(3) | 1.95(1) | N(3)−C(32) | 1.43(3) | O(11)−C(14) | 1.51(3) | C(16)−C(17) | 1.49(3) |
| Cu−O(4) | 1.93(1) | N(4)−C(30) | 1.48(3) | O(11)−C(18) | 1.54(3) | C(18)−C(19) | 1.70(5) |
| Cu−N(1) | 2.10(2) | N(4)−C(33) | 1.46(3) | C(18)−C(20) | 1.52(5) | C(21)−C(22) | 1.57(3) |
| Cu−N(3) | 2.09(2) | N(4)−C(34) | 1.42(3) | C(22)−C(23) | 1.55(3) | C(28)−C(29) | 1.48(3) |
| C29−C(30) | 1.59(3) | | | | | | |

#### Bond Angles

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(6)−Pr−O(7) | 79.8(5) | O(6)−Pr−O(8) | 69.3(5) | O(5)−C(4)−C(5) | 122(3) | C(3)−C(4)−C(5) | 125(3) |
| O(6)−Pr−O(9) | 94.1(5) | O(6)−Pr−O(10) | 92.5(5) | C(4)−C(5)−C(6) | 130(3) | O(6)−C(6)−C(5) | 119(3) |
| O(7)−Pr−O(8) | 68.8(5) | O(7)−Pr−O(9) | 141.8(5) | C(14)−O(11)−C(18) | 117(2) | O(6)−C(6)−C(7) | 121(3) |
| O(7)−Pr−O(10) | 142.2(5) | O(8)−Pr−O(9) | 73.8(5) | C(16)−O(12)−C(18) | 118(2) | C(5)−C(6)−C(7) | 118(3) |
| O(3)−Pr−O(4) | 64.1(4) | O(8)−Pr−O(10) | 142.4(4) | O(8)−C(9)−C(8) | 112(2) | O(8)−C(9)−C(10) | 125(3) |
| O(3)−Pr−O(5) | 132.5(5) | O(9)−Pr−O(10) | 75.2(5) | C(8)−C(9)−C(10) | 121(3) | C(21)−N(1)−C(24) | 113(2) |
| O(3)−Pr−O(6) | 143.9(4) | O(3)−Pr−O(7) | 83.0(5) | C(9)−C(10)−C(11) | 121(3) | C(21)−N(1)−C(25) | 106(2) |
| O(3)−Pr−O(8) | 74.9(4) | O(3)−Pr−O(9) | 80.4(5) | O(7)−C(11)−C(10) | 129(4) | C(24)−N(1)−C(25) | 109(2) |
| O(3)−Pr−O(10) | 119.7(5) | O(4)−Pr−O(5) | 75.3(5) | O(9)−C(14)−O(11) | 112(2) | C(23)−N(2)−C(26) | 108(2) |
| O(1)−Cu−O(3) | 101.5(7) | O(4)−Pr−O(6) | 144.2(5) | O(9)−C(14)−C(13) | 108(2) | C(23)−N(2)−C(27) | 109(2) |
| O(1)−Cu−O(4) | 105.1(6) | O(4)−Pr−O(7) | 85.0(5) | O(9)−C(14)−C(15) | 114(2) | C(26)−N(2)−C(27) | 118(2) |
| O(1)−Cu−N(1) | 91.4(8) | O(4)−Pr−O(8) | 133.6(4) | O(11)−C(14)−C(13) | 103(2) | O(11)−C(14)−C(15) | 112(2) |
| O(1)−Cu−N(3) | 93.8(8) | O(4)−Pr−O(9) | 117.2(5) | C(13)−C(14)−C(15) | 107(2) | C(14)−C(15)−C(16) | 116(2) |
| O(3)−Cu−O(4) | 81.4(6) | O(4)−Pr−O(10) | 80.0(4) | O(10)−C(16)−O(12) | 111(2) | O(10)−C(16)−C(15) | 114(2) |
| O(3)−Cu−N(1) | 84.1(7) | O(5)−Pr−O(6) | 69.0(5) | O(10)−C(16)−C(17) | 113(2) | O(12)−C(16)−C(15) | 108(2) |
| O(3)−Cu−N(3) | 161.5(7) | O(5)−Pr−O(7) | 69.4(5) | O(12)−C(16)−C(17) | 100(2) | C(15)−C(16)−C(17) | 111(2) |
| O(4)−Cu−N(1) | 159.9(7) | O(5)−Pr−O(8) | 124.7(5) | O(11)−C(18)−O(12) | 113(3) | O(11)−C(18)−C(19) | 108(3) |
| O(4)−Cu−N(3) | 84.7(6) | O(5)−Pr−O(9) | 143.1(5) | O(11)−C(18)−C(20) | 101(3) | O(12)−C(18)−C(19) | 114(3) |
| N(1)−Cu−N(3) | 106.0(8) | O(5)−Pr−O(10) | 73.2(5) | O(12)−C(18)−C(20) | 109(3) | C(19)−C(18)−C(20) | 110(3) |
| Pr−O(3)−Cu | 100.9(5) | C(28)−N(3)−C(31) | 110(2) | N(1)−C(21)−C(22) | 107(2) | O(3)−C(22)−C(21) | 114(2) |
| C(28)−N(3)−C(32) | 107(2) | C(31)−N(3)−C(32) | 112(2) | O(3)−C(22)−C(23) | 110(2) | C(21)−C(22)−C(23) | 105(2) |
| Pr−O(4)−Cu | 101.4(5) | C(30)−N(4)−C(33) | 113(2) | N(2)−C(23)−C(22) | 117(2) | N(3)−C(28)−C(29) | 114(2) |
| C(30)−N(4)−C(34) | 109(2) | C(33)−N(4)−C(34) | 110(2) | O(4)−C(29)−C(28) | 110(2) | O(4)−C(28)−C(30) | 108(2) |
| O(1)−C(1)−O(2) | 135(4) | O(5)−C(4)−C(3) | 112(3) | C(28)−C(29)−C(30) | 110(2) | N(4)−C(30)−C(29) | 117(2) |

### (c) Compound 3a
#### Bond Lengths

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Nd−O(1) | 2.36(1) | Nd−O(2) | 2.44(2) | N(2)−C(3) | 1.45(3) | N(2)−C(6) | 1.45(3) |
| Nd−O(3) | 2.75(1) | Nd−O(4) | 2.52(2) | O(1)−C(2) | 1.39(2) | N(2)−C(7) | 1.45(3) |
| Nd−O(5) | 2.56(2) | Nd−O(6) | 2.56(2) | C(1)−C(2) | 1.52(3) | N(3)−C(8) | 1.48(3) |
| Nd−O(7) | 2.49(2) | Nd−O(8) | 2.49(1) | C(2)−C(3) | 1.51(3) | N(3)−C(11) | 1.49(3) |
| Nd−N(2) | 2.83(2) | Cu(1)−O(1) | 1.92(1) | C(8)−C(9) | 1.55(3) | N(3)−C(12) | 1.44(3) |
| Cu(1)−O(3) | 1.96(1) | Cu(1)−O(11) | 1.95(2) | C(9)−C(10) | 1.56(3) | N(4)−C(10) | 1.49(3) |

**Table 3** (Continued)

(c) Compound **3a**

Bond Lengths

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu(1)−N(1) | 2.06(2) | O(2)−C(9) | 1.40(2) | C(15)−C(16) | 1.55(3) | N(4)−C(13) | 1.50(3) |
| Cu(2)−O(2) | 1.91(1) | O(3)−C(16) | 1.39(2) | C(16)−C(17) | 1.51(3) | N(4)−C(14) | 1.47(3) |
| Cu(2)−O(3) | 1.98(1) | O(4)−C(23) | 1.23(2) | C(22)−C(23) | 1.59(4) | N(5)−C(15) | 1.44(3) |
| Cu(2)−O(10) | 1.97(2) | O(5)−C(25) | 1.26(3) | C(23)−C(24) | 1.38(3) | N(5)−C(18) | 1.48(3) |
| Cu(2)−N(3) | 2.02(2) | O(6)−C(27) | 1.28(3) | C(24)−C(25) | 1.37(3) | N(5)−C(19) | 1.46(3) |
| O(7)−C(27) | 1.24(3) | O(8)−C(29) | 1.25(3) | C(25)−C(26) | 1.62(4) | N(6)−C(17) | 1.43(3) |
| O(9)−C(29) | 1.21(3) | O(10)−C(31) | 1.28(3) | C(27)−C(28) | 1.50(4) | N(6)−C(20) | 1.46(3) |
| O(11)−C(31) | 1.20(3) | N(1)−C(1) | 1.44(3) | C(29)−C(30) | 1.53(4) | N(6)−C(21) | 1.46(3) |
| N(1)−C(4) | 1.45(3) | N(1)−C(5) | 1.48(3) | C(31)−C(32) | 1.54(3) | | |

Bond Angles

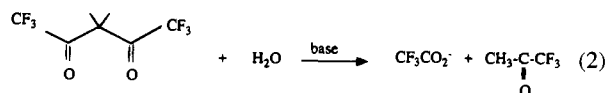| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)−Nd−O(2) | 112.6(5) | O(2)−Nd−N(2) | 62.0(5) | O(3)−Cu(2)−O(10) | 95.1(6) | C(3)−N(2)−C(6) | 111(2) |
| O(1)−Nd−O(3) | 61.9(4) | O(3)−Nd−O(4) | 83.1(5) | O(3)−Cu(2)−N(3) | 175.0(8) | C(3)−N(2)−C(7) | 108(2) |
| O(1)−Nd−O(4) | 80.3(5) | O(3)−Nd−O(5) | 88.8(5) | O(10)−Cu(2)−N(3) | 89.9(8) | C(6)−N(2)−C(7) | 109(2) |
| O(1)−Nd−O(5) | 139.6(5) | O(3)−Nd−O(6) | 150.5(5) | Nd−O(1)−Cu(1) | 110.6(6) | Cu(2)−N(3)−C(8) | 103(2) |
| O(1)−Nd−O(6) | 124.7(5) | O(3)−Nd−O(7) | 145.7(5) | Nd−O(1)−C(2) | 131(1) | Cu(2)−N(3)−C(11) | 114(2) |
| O(1)−Nd−O(7) | 139.3(5) | O(3)−Nd−O(8) | 96.9(5) | Cu(1)−O(1)−C(2) | 112(1) | Cu(2)−N(3)−C(12) | 114(2) |
| O(1)−Nd−O(8) | 77.0(5) | O(3)−Nd−N(2) | 123.7(5) | Nd−O(2)−Cu(2) | 108.6(7) | C(8)−N(3)−C(11) | 106(2) |
| O(1)−Nd−N(2) | 62.0(5) | O(4)−Nd−O(5) | 68.3(5) | Nd−O(2)−C(9) | 130(1) | C(8)−N(3)−C(12) | 111(2) |
| O(2)−Nd−O(3) | 61.8(4) | O(4)−Nd−O(6) | 71.1(5) | Cu(2)−O(2)−C(9) | 112(1) | C(11)−N(13)−C(12) | 108(2) |
| O(2)−Nd−O(4) | 125.0(5) | O(4)−Nd−O(7) | 121.6(6) | Nd−O(3)−Cu(1) | 95.3(5) | C(10)−N(4)−C(13) | 104(2) |
| O(2)−Nd−O(5) | 69.9(5) | O(4)−Nd−O(8) | 154.1(5) | Nd−O(3)−Cu(2) | 95.7(5) | C(10)−N(4)−C(14) | 114(2) |
| O(2)−Nd−O(6) | 122.6(5) | O(4)−Nd−N(2) | 83.1(5) | Nd−O(3)−C(16) | 133(1) | C(13)−N(4)−C(14) | 111(2) |
| O(2)−Nd−O(7) | 83.9(5) | O(5)−Nd−O(6) | 68.7(5) | Cu(1)−O(3)−Cu(2) | 106.8(7) | C(15)−N(5)−C(18) | 114(2) |
| O(2)−Nd−O(8) | 76.0(5) | O(5)−Nd−O(7) | 80.4(6) | C(15)−N(5)−C(19) | 108(2) | N(6)−C(17)−C(16) | 112(2) |
| O(5)−Nd−O(8) | 137.5(5) | Cu(1)−O(3)−C(16) | 112(1) | C(18)−N(5)−C(19) | 109(2) | O(4)−C(23)−C(22) | 112(2) |
| O(5)−Nd−N(2) | 133.9(5) | Cu(2)−O(3)−C(16) | 111(1) | C(17)−N(6)−C(20) | 112(2) | O(4)−C(23)−C(24) | 133(2) |
| O(6)−Nd−O(7) | 51.5(6) | Nd−O(4)−C(23) | 131(2) | C(17)−N(6)−C(21) | 110(2) | C(22)−C(23)−C(24) | 116(2) |
| O(6)−Nd−O(8) | 112.6(5) | Nd−O(5)−C(25) | 132(2) | C(20)−N(6)−C(21) | 105(2) | C(23)−C(24)−C(25) | 120(2) |
| O(6)−Nd−N(2) | 68.2(5) | Nd−O(6)−C(27) | 91(2) | N(1)−C(1)−C(2) | 112(2) | O(5)−C(25)−C(24) | 130(3) |
| O(7)−Nd−O(8) | 71.3(6) | Nd−O(7)−C(27) | 96(2) | O(1)−C(2)−C(1) | 113(2) | O(5)−C(25)−C(26) | 113(3) |
| O(7)−Nd−N(2) | 85.4(6) | Nd−O(8)−C(29) | 122(2) | O(1)−C(2)−C(3) | 111(2) | C(24)−C(25)−C(26) | 117(3) |
| O(8)−Nd−N(2) | 75.5(5) | Cu(2)−O(10)−C(31) | 127(2) | C(1)−C(2)−C(3) | 113(2) | O(6)−C(27)−O(7) | 121(3) |
| O(1)−Cu(1)−O(3) | 86.4(6) | Cu(1)−N(1)−C(1) | 105(2) | N(2)−C(3)−C(2) | 114(2) | O(6)−C(27)−C(28) | 118(3) |
| O(1)−Cu(1)−O(11) | 174.7(7) | Cu(1)−N(1)−C(4) | 114(2) | N(3)−C(8)−C(9) | 110(2) | O(7)−C(27)−C(28) | 121(3) |
| O(1)−Cu(1)−N(1) | 86.8(7) | Cu(1)−N(1)−C(5) | 109(2) | O(2)−C(9)−C(8) | 109(2) | O(8)−C(29)−O(9) | 130(3) |
| O(3)−Cu(1)−O(11) | 96.2(6) | C(1)−N(1)−C(4) | 110(2) | O(2)−C(9)−C(10) | 111(2) | O(8)−C(29)−C(30) | 113(2) |
| O(3)−Cu(1)−N(1) | 170.6(7) | C(1)−N(1)−C(5) | 112(2) | C(8)−C(9)−C(10) | 107(2) | O(9)−C(29)−C(30) | 117(3) |
| O(11)−Cu(1)−N(1) | 90.2(7) | C(4)−N(1)−C(5) | 107(2) | N(4)−C(10)−C(9) | 116(2) | O(10)−C(31)−O(11) | 132(2) |
| O(2)−Cu(2)−O(3) | 87.1(6) | Nd−N(2)−C(3) | 106(1) | N(5)−C(15)−C(16) | 112(2) | O(10)−C(31)−C(32) | 112(2) |
| O(2)−Cu(2)−O(10) | 174.2(7) | Nd−N(2)−C(6) | 109(1) | O(3)−C(16)−C(15) | 110(2) | O(11)−C(31)−C(32) | 116(2) |
| O(2)−Cu(2)−N(3) | 87.9(8) | Nd−N(2)−C(7) | 115(2) | O(3)−C(16)−C(17) | 109(2) | C(15)−C(16)−C(17) | 113(2) |
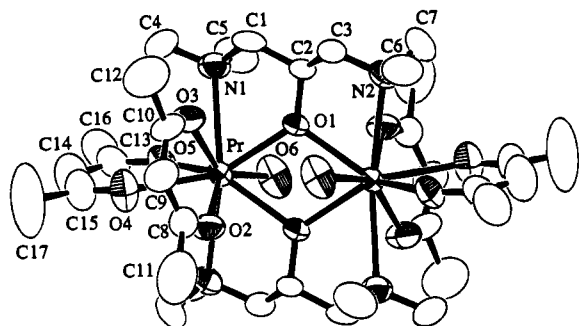


**Figure 1.** ORTEP diagram for compound **1** with 50% thermal ellipsoids and the labeling scheme. The THF groups and the fluorine atoms were omitted for clarity.

roacetate ligand with a relatively long Cu−O bond (Cu−O(1) = 2.23(2) Å). The Cu(II) geometry is therefore square-pyramidal. Since no trifluoroacetate was used in the reaction, we believed that the trifluoroacetate ligand is one of the decomposition products of the hfacac ligand (eq 2). β-Diketones



$$CF_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CF_3 \ + \ H_2O \ \xrightarrow{\text{base}} \ CF_3CO_2^- \ + \ CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CF_3 \quad (2)$$

have been known to undergo the retro-Claisen condensation reaction to produce a ketone and a carboxylate when strong bases such as alkaline metal hydroxides are present (eq 2).[11]
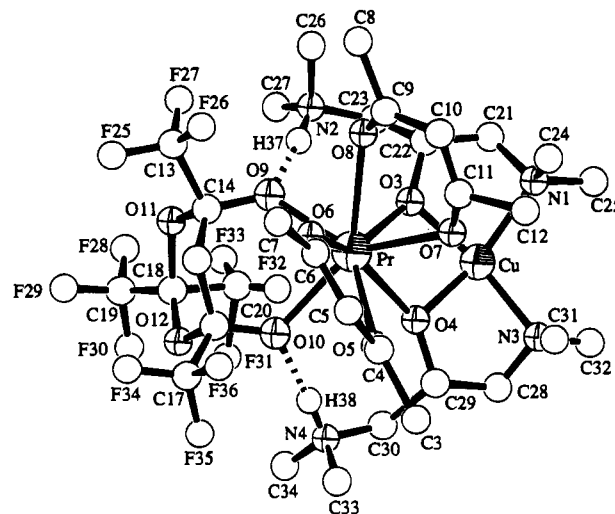
**Figure 2.** ORTEP diagram for compound **2a** with the labeling scheme. For clarity, all atoms are shown as ideal spheres. Fluorine atoms except those on the L ligand and the trifluoroacetate ligand on the copper center were omitted.

The decomposition of β-diketonato ligands in metal complexes with alkoxy ligands has also been observed previously and was attributed to the presence of the trace amount of $H_2O$ and the alkoxy ligand in the reaction medium.[12] Both the methoxy and the bdmapH ligand in the synthesis of **2** could function as the base to promote the decomposition of the hfacacH molecule.
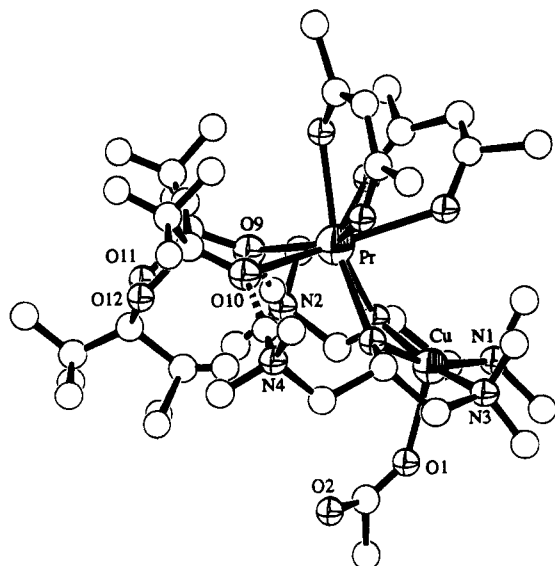
**Figure 3.** Side view of compound **2a** showing the coordination geometry of the metal ions.
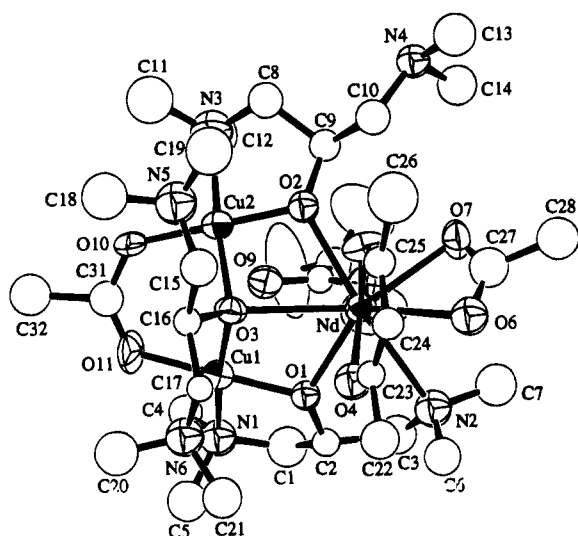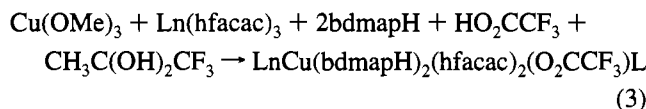


**Figure 4.** ORTEP diagram for compound **3a** with 50% thermal ellipsoids and the labeling scheme. The noncoordinating hfacacH, the THF, and the fluorine atoms on the hfacac ligand were omitted for clarity.

The Pr(III) center is surrounded by eight oxygen atoms with typical Pr—O bond lengths, four from two hfacac ligands, two from the bdmapH ligands, and two from the ligand L, 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato. The ligand L can be considered as a derivative of 1,3-dioxane-4,6-diol. As shown in structures **A**, it has a chair conformation with 4,6-



**A**
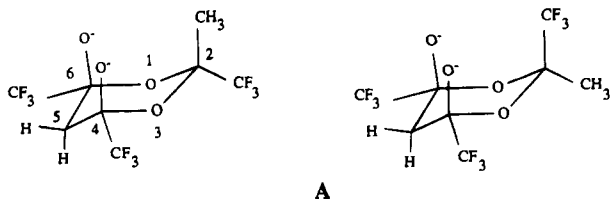
trifluoromethyl groups occupying the equatorial positions and the two oxygen atoms occupying the axial positions. The trifluoromethyl group and the methyl group at the 2 positions are disordered with a 50% occupancy for both *a* and *e* positions. We believe that the ligand L is the result of cycloaddition of 1,1,1-trifluoro-2,2-propanediol to the hfacac ligand promoted by the metal complex and the amino groups on the bdmapH

ligand. The 1,1,1-trifluoro-2,2-propanediol is the hydration product[8] of trifluoroacetone, the other decomposition product of the hfacac ligand (eq 2). In fact, compound **2** was obtained by the modified reaction where 1,1,1-trifluoroacetone and $H_2O$ were employed (eq 3). The adventitious $H_2O$ molecule in the

$$Cu(OMe)_3 + Ln(hfacac)_3 + 2bdmapH + HO_2CCF_3 +$$
$$CH_3C(OH)_2CF_3 \rightarrow LnCu(bdmapH)_2(hfacac)_2(O_2CCF_3)L$$
$$(3)$$

original synthesis is believed to come from either the solvent or the bdmapH reagent which is difficult to be purified and totally free of water. The amino groups on the bdmap ligand appeared to function as a Lewis base to remove the protons on the diol, thereby increasing its nucleophilicity and stabilizing the product. Crystallographic data seems to support this. In compound **2a**, the bdmapH ligand has a zwitterion form with one of the amino groups being coordinated to the copper center and the other one being protonated. The protonated amino groups form hydrogen bonds with the two oxygen atoms of the L ligand is evidenced by the N(2)$\cdots$O(9) distance of 2.74(3) Å and the N(4)$\cdots$O(10) distance of 2.69(3) Å. A similar zwitterion form of the bdmapH ligand has been observed in the dinuclear complex[9] $Cu^{II}_2(bdmapH)_2Cl_4$.

1,3-dioxane and substituted 1,3-dioxane compounds with the hydroxy group at the 4 or 5 position can be synthesized by the reaction of aldehydes or ketones with appropriate alcohols.[13] In contrast, 1,3-dioxane-4,6-diol compounds are very rare due to their tendency to dissociate back to $\beta$-diketone and the corresponding diol. To our knowledge, 1,3-dioxane-4,6-diols with or without substituents are previously unknown. Although the electron-withdrawing trifluoromethyl groups on the ligand L can contribute to the stability of this ligand, the metal centers are also believed to play an important role in the formation of the L ligand because independent syntheses of the L ligand in the absence of the metal complexes were unsuccessful. At-

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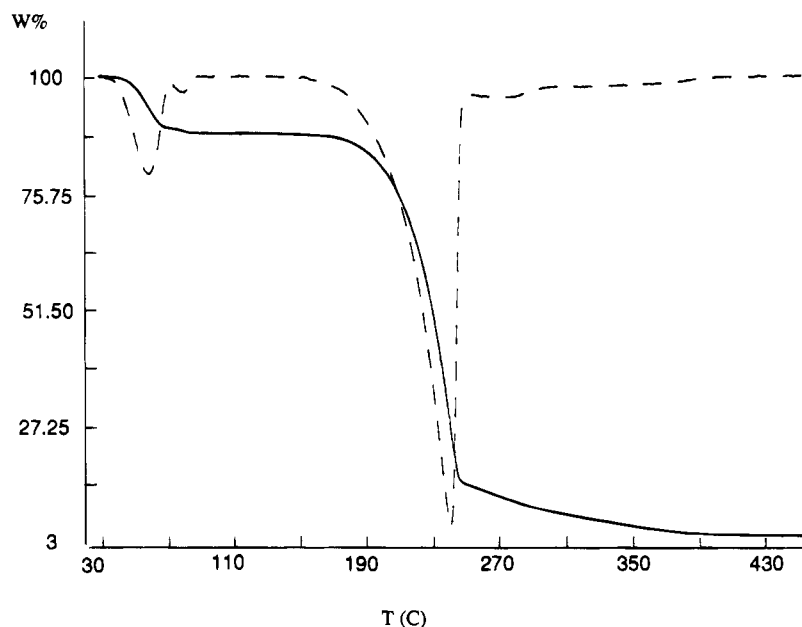
**Figure 5.** TGA diagram for **1**. The dashed line is the first derivative of the percentage of weight loss.
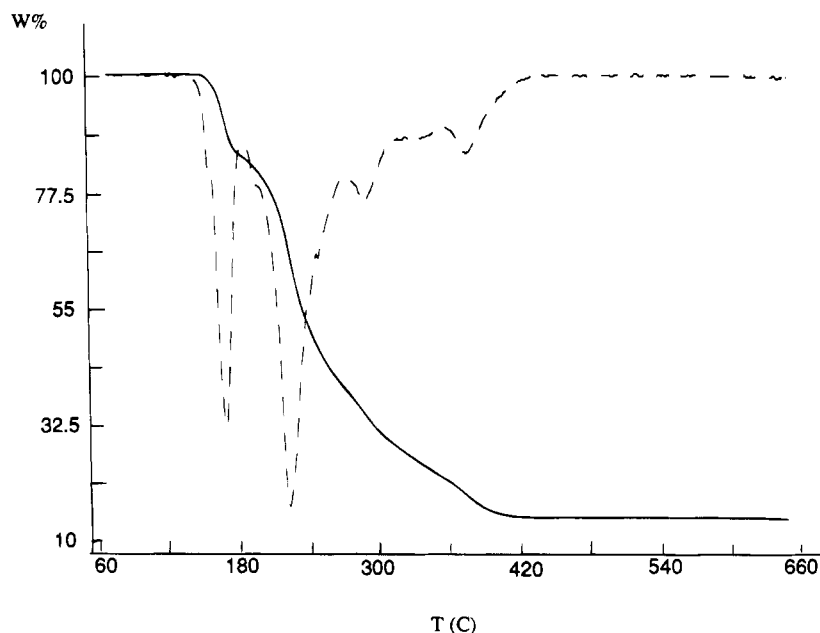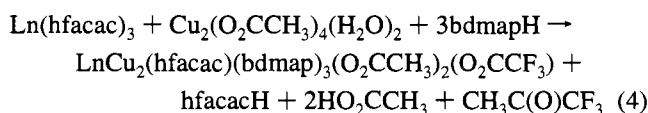


**Figure 6.** TGA diagram for **2b**. The dashed line is the first derivative of the percentage of weight loss.

tempts to free the ligand L from the complex by the addition of acids have not been successful perhaps due to the decomposition of ligand L under such conditions. Hexafluoroacetone hydrate $CF_3C(OH)_2CF_3$ has been known to undergo a self-condensation reaction in the presence of a transition metal complex.[14] A template—condensation process has been proposed for such reactions.[14a] The $CF_3C(OH)_2CH_3$ condensation reaction with the hfacac ligand described here may have proceeded by a similar fashion. The Cu(II) center is believed to play an important role because the L ligand was not observed when only yttrium or lanthanide complexes were employed in the reaction such as in the synthesis of compound **1**. Nucleophilic addition reactions of alkoxy groups to fluorinated acetylacetonato ligands have been reported previously. For example, the hfacac ligand in a cobalt(III) complex has been reported to undergo a reversible-addition reaction with a methoxy ligand.[15] However, the double-addition reaction by two alkoxy ligands or the cycloaddition reaction by a diol observed in **2** are previously unknown, although the double-

addition reaction by hydroxy ligands to $\beta$-diketones has been well established.[16]

**Synthesis and Structure of $NdCu_2(hfacac)(bdmap)_3(O_2$-$CCH_3)_2(O_2CCF_3)(hfacacH)(THF)$ (3a).** Compound **3a** was obtained readily in good yield from the reaction of $Nd(hfacac)_3$ with $Cu_2(O_2CCH_3)_4(H_2O)_2$ and bdmapH in a 1:1:3 ratio in THF. The composition and structure of this compound has been established by X-ray diffraction and elemental analyses. A THF solvent molecule and a neutral hfacacH molecule co-crystallized with the product. The stoichiometry of the reaction is given in eq 4. The trifluoroacetate ligand in this complex is believed

$$Ln(hfacac)_3 + Cu_2(O_2CCH_3)_4(H_2O)_2 + 3bdmapH \rightarrow$$
$$LnCu_2(hfacac)(bdmap)_3(O_2CCH_3)_2(O_2CCF_3) +$$
$$hfacacH + 2HO_2CCH_3 + CH_3C(O)CF_3 \quad (4)$$

again to be one of the decomposition products of the hfacac ligand. In the synthesis of compound **3**, there was no alkoxy source in the starting material and the bdmap ligand was the
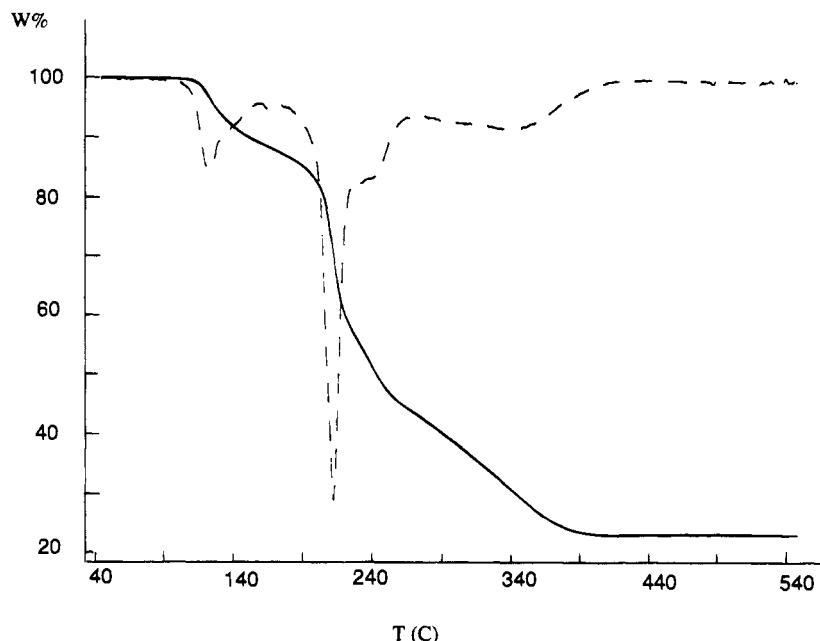
**Figure 7.** TGA diagram for **3a**. The dashed line is the first derivative of the percentage of weight loss.

only Lewis base present. Yet, interestingly, the cleavage of the hfacac ligand occurred again. In fact we have observed that in the absence of metal complexes, the addition of tetramethylpropanediamine (tmpda) and $H_2O$ to the THF solution of hexafluoroacetylacetone caused nearly quantitatively decomposition of the hfacacH molecule and the [tmpdaH$_2$][O$_2$-CCF$_3$]$_2$ salt was isolated quantitatively. The facile decomposition of the hfacac ligand can be attributed to the electron-withdrawing CF$_3$ groups which make the hfacac ligand susceptible to nucleophiles such as $H_2O$.

Selected atomic positional and thermal parameters are listed in Table 2c. Important bond lengths and angles are given in Table 3c. An ORTEP diagram for the molecule of **3a** is shown in Figure 4. The three metal ions in **3a** are bridged by three bdmap ligands through the oxygen atoms in a triangular arrangement with the Cu(1)—Cu(2), Nd—Cu(1), and Nd—Cu(2) distances being 3.165(5), 3.525(3), and 3.546(3) Å, respectively. Similar structural features have also been observed in the complex[4] LaCu$_2$(bdmap)$_3$(O$_2$CCF$_3$)$_4$. The O(3) atom of one of the bdmap ligands functions as a triply-bridging ligand and is bonded to all three metal ions. A similar bonding mode of the bdmap ligand has been observed previously in the complex[9] of Cu$_3$(bdmap)$_2$Cl$_4$. Each copper center is coordinated by three oxygen atoms and one nitrogen atom with normal bond lengths and an approximate square-planar geometry. The O(9) atom of the trifluoroacetate ligand and the N(6) and N(5) atoms of a bdmap ligand occupy the fifth and the sixth positions of the two copper atoms as indicated by the distances Cu(1)—O(9) = 2.69(2), Cu(2)—O(9) = 2.68(2), Cu(1)—N(6) = 2.53(2), and Cu(2)—N(5) = 2.66(2) Å. The geometry of the copper atoms, therefore, can be best described as an elongated octahedron. The Nd atom is surrounded by one nitrogen atom and eight oxygen atoms, three from the bdmap ligands, two from the acetate ligand, one from the trifluoroacetate ligand (O(8)), and two from the hfacac ligand (O(4) and O(5)). The N(2) atom is weakly bonded to the Nd center as evidenced by the long Nd—N(2) distance of 2.83(2) Å. One of the amino groups of the bdmap ligands, N(4), is not coordinated to any metal center, and its lone pair is oriented away from the complex. We believe that the N(4) atom forms two hydrogen bonds with the oxygen atoms of the non-coordinating hfacacH molecule in the lattice as evidenced by the N(4)—O(12) and N(4)—O(13) distances, 2.71 and 2.84 Å. The position of the proton could not be
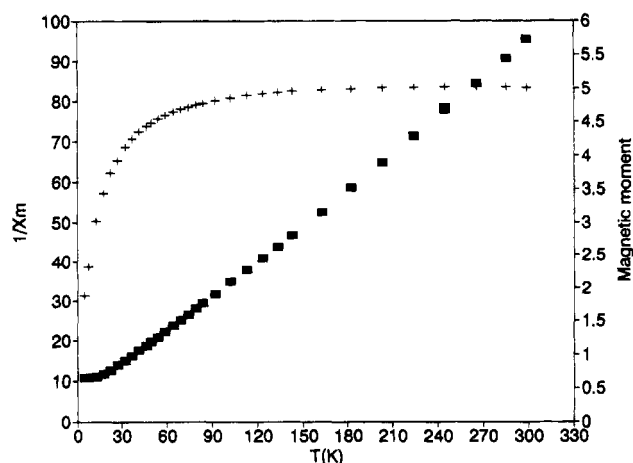


**Figure 8.** Plots of $\chi_m^{-1}$ (filled square) and magnetic moment (cross) of compound **1** vs temperature.

located, but it is likely that the proton is bonded to the N(4) atom. $\beta$-Diketones have been known to exist in both ketone and enol resonance forms.[11] The noncoordinating HfacacH ligand in **3a** has the enol form, as indicated by the C—C—C bond angle of 118(3)° and the C—C bond lengths of 1.42(3) and 1.33(4) Å (structure **B**). The enolate form of the hfacacH molecule in **3a** is apparently stabilized by the electron-withdrawing group CF$_3$ and the formation of hydrogen bonds with the amino group.



**B**
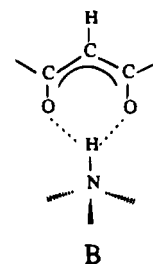
**Thermogravimetric Analysis of Compounds 1—3.** The thermal behaviors of compounds **1—3** have been examined by thermogravimetric analysis under 1 atm of oxygen. TGA diagrams for compounds **1**, **2b**, and **3a** are given in Figures
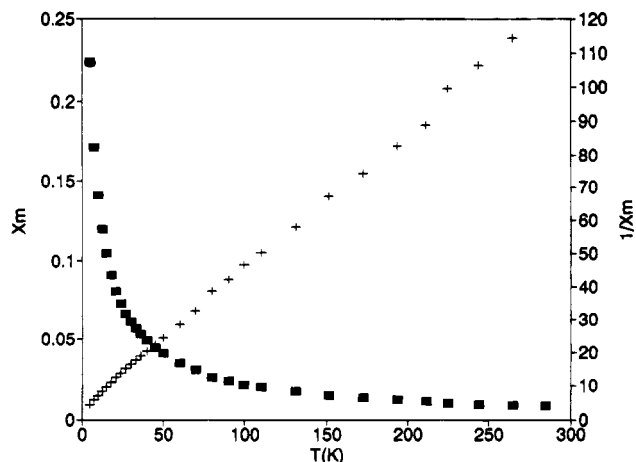
**Figure 9.** Plots of $\chi_m$ (filled square) and $\chi_m^{-1}$ (cross) of compound **3b** vs temperature.
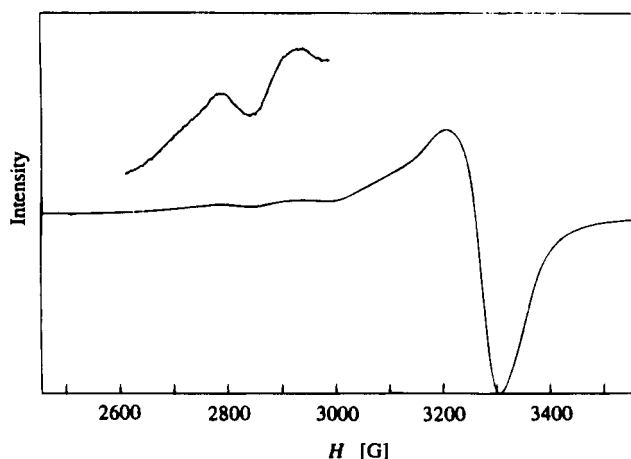


**Figure 10.** Polycrystalline powder EPR spectrum of **2b** at 77 K.

5—7, respectively. Upon heating, compound **1** initially loses the THF molecule in the temperature range 40—70 °C, and the residual weight is about 91% of the parent molecule. Further heating results in the loss of the $H_2O$ molecule, and the residual weight corresponds to 89% of compound **1**. At the temperature range of 190—250 °C, a rapid weight loss occurs and the final residual weight is only about 3% of the original weight. We believe that this weight loss is due to the sublimation of the residual sample $Pr_2(bdmap)_2(hfacac)_4$. Indeed, when compound **1** was heated under vacuum (0.5 mmHg), the sublimation occurred at 120 °C. The nonzero residual weight in the TGA diagram of **1** is probably due to the decomposition of a small percentage of the sample under the experimental conditions. Compound **2b** undergoes several stages of decomposition in the temperature range of 130—360 °C. The final residual weight of the decomposed sample was 15% of that of compound **2b** which corresponds to the formula of $YCuO_{2.5}$. The vacuum

dried sample of compound **3a** also undergoes several stages of decomposition in the temperature range of 110—400 °C. After 400 °C, a constant residual weight, 24% of the formula weight of $NdCu_2(bdmap)_3(O_2CCH_3)_2(O_2CCF_3)(hfacac)(hfacacH)$, is achieved which is consistent with the formula of $NdCu_2O_{3.5}$.

**Magnetic Properties of Compounds 1, 2b, and 3b.** Compounds **1** and **3b** are essentially paramagnetic as shown by the magnetic susceptibility data collected over the temperature range 4—300 K (Figure 8 and 9). The plot of $\chi_m^{-1}$ vs $T$ for compound **1** is almost a straight line except the small deviation at low temperature region which is apparently caused by the weak magnetic exchange between the two Pr(III) centers.[17a] The structure of the $Cu_2$ portion in **3b** resembles that in La-$Cu_2(bdmap)_3(O_2CCF_3)_4$, which has been found to have an antiferromagnetically coupled ground state.[4] The plot of $\chi_m^{-1}$ vs $T$ for compound **3b** is essentially a straight line, indicating that the magnetism of **3b** is dominated by the paramagnetism of Pr(III). The small deviation can be attributed to the weak Pr(III)—Cu(II) magnetic exchange.[17b,17c]

Compound **2b** is paramagnetic due to the paramagnetic Cu(II) ion. The polycrystalline powder EPR spectrum of **2b** recorded at the X-band frequencies and 77 K is shown in Figure 10. There are two low field $g_{\parallel}$ peaks and one high field $g_{\perp}$ peak, which indicate some overlaps between $g_{\parallel}$ transitions and $g_{\perp}$ transitions. The value of hyperfine constant $A_{\parallel}$ is 145 G while $g_{\parallel} = 2.24$ and $g_{\perp} = 2.05$.

**Conclusions**

The hfacac ligand has a complicated reactivity in the presence of the metal ions and Lewis base. Lanthanide and copper complexes with bdmap and hfacac ligands can have favorable thermal properties. They can either be readily sublimed or thermally decomposed to the corresponding oxides, which along with their high solubility in organic solvents makes these compounds possible candidates as precursors for ceramic applications.

(17) (a) Liu, S.; Gelmini, L.; Rettig, S. J.; Thompson, R. C.; and Orvig, C. *J. Am. Chem. Soc.* **1992**, *114*, 6081. (b) Bouyad, A.; Brouca-Cabarrecq, C.; Trombe, J.-C. *Inorg. Chim. Acta* **1992**, *55*, 2447. (c) Benelli, C.; Caneshi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750.