Inorg. Chem. **1993,** *32,* 4992–4993

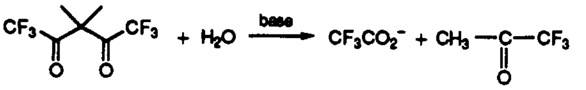
Synthesis and Crystal Structure of A Dinuclear Yttrium(III)- (Lanthanide(III)-) Copper(II) Complex with an Unusual 2-Methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato Ligand

Suning Wang,* Zhen Pang, and Karen D. L. Smith

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

Received June 10, 1993

Acetylacetonato and substituted acetylacetonato ligands have been frequently employed in the synthesis of homo and heteronuclear molecular precursor complexes for ceramic materials due to the high solubility and volatility of the resulting complexes.[1] Most of the current research in this area has been focused on the characterization of the structures and physical properties of the precursor complexes. In contrast, the investigation on the chemical reactivity of this class molecules has been rather limited. Recent study has shown that acetylacetonato and substituted acetylacetonato ligands bonded to a yttrium or lanthanide ion readily undergo decomposition to produce carboxylates in the presence of a Lewis base such as metal alkoxides or amino alcohol ligands.[2] It has been proposed that this decomposition reaction could be explained by the retro-Claisen condensation reactions[3] of β-diketones induced by Lewis bases and the trace amount of H_2O in the reaction medium as shown in eq 1. However, the



(1)

ketone product from the proposed retro-Claisen type reaction has not been observed in these previously investigated systems. We report here a dinuclear Ln^{III}–Cu^{II} complex with an unprecedentated 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato ligand produced by the unusual condensation of the trifluoroacetone hydrate with a hfacac ligand in this system.

The Ln^{III}–Cu^{II} (Ln = Y, Pr) dinuclear complex **1** was initially isolated as a blue crystalline product in low yield along with the major product[4] $Ln_2(bdmap)_2(hfacac)_4(H_2O)_2(THF)_2$ from the reaction of $Cu(OMe)_2$, $Ln(hfacac)_3$, and bdmapH (bdmapH = 1,3-bis(dimethylamino)-2-propanol) in a 1:1:2 ratio in THF at 23 °C, attempted for the synthesis of the $LnCu(bdmap)_2(hfacac)_3$ compound. Single-crystal X-ray diffraction and elemental analyses[5] unambiguously established that compound **1** has the formula $Ln^{III}Cu^{II}(bdmapH)_2(hfacac)_2(O_2CCF_3)L$ (Ln = Y (**1a**), Ln = Pr (**1b**); L = 2-methyl-2,4,6-tris(trifluoromethyl)-1,3-dioxane-4,6-diolato). Compounds **1a** and **1b** have the same structures in the solid state. The structure of **1b** and important bond lengths and angles are given in Figure 1. The Cu(II) and Ln(III) ions are bridged by two oxygen atoms from the two bdmapH ligands and separated by 3.357(3) Å. Similar Cu–Ln separations have been observed previously.[1a,6] 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 trifluoroacetate ligand with a relatively long Cu–O bond (2.21(2) Å). The Cu(II) geometry is therefore square-pyramidal. The Ln(III) center is surrounded by eight oxygen atoms with typical Ln–O bond lengths, four from two hfacac ligands, two from the bdmapH ligand, and two from the unusual ligand L.

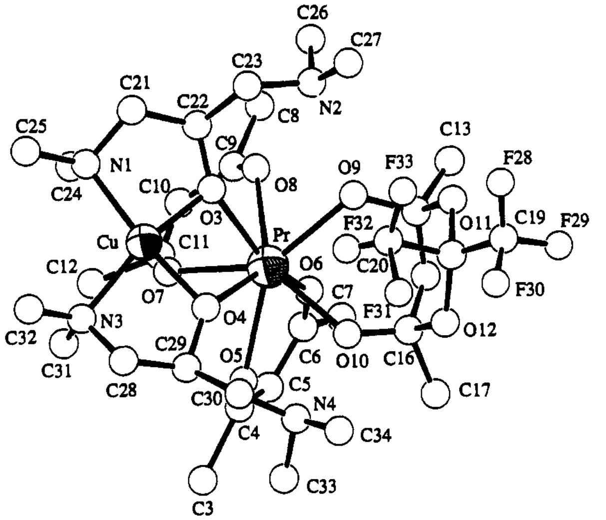


Figure 1. ORTEP diagram for compound **1b** with the labeling scheme. For clarity, the trifluoroacetate ligand bonded to the copper atom and fluorine atoms except those bonded to C(18) were not shown. Selected bond lengths (Å) and angles (deg): Pr–O(3) = 2.40(1), Pr–O(4) = 2.40(1), Pr–O(5) = 2.55(2), Pr–O(6) = 2.47(2), Pr–O(7) = 2.51(2), Pr–O(8) = 2.60(1), Pr–O(9) = 2.41(1), Pr–O(10) = 2.46(1), Cu–O(1) = 2.21(2), Cu–O(3) = 1.94(2), Cu–O(4) = 1.91(2), Cu–N(1) = 2.10(2), Cu–N(3) = 2.08(2), C(14)–O(9) = 1.39(3), C(16)–O(10) = 1.33(3), C(14)–C(15) = 1.47(3), C(15)–C(16) = 1.50(3), C(14)–O(11) = 1.50(3), C(16)–O(12) = 1.51(3), C(18)–O(11) = 1.56(5), C(18)–O(12) = 1.57(5), C(18)–C(19) = 1.42(5), C(18)–C(20) = 1.50(7); O(3)–Pr–O(4) = 63.8(5), O(5)–Pr–O(6) = 68.8(5), O(7)–Pr–O(8) = 68.2(5), O(9)–Pr–O(10) = 75.0(5), O(3)–Cu–O(4) = 82.3(6), N(1)–Cu–N(3) = 105.4(8), O(1)–Cu–N(1) = 84.4(7), O(1)–Cu–N(3) = 92.8(8), O(9)–C(14)–C(15) = 113(1), O(9)–C(14)–O(11) = 112(2), O(9)–C(14)–C(13) = 107(1), C(14)–C(15)–C(16) = 116(1), O(10)–C(16)–C(15) = 113(2), O(10)–C(16)–O(12) = 109(1), O(10)–C(16)–C(17) = 112(2), C(19)–C(18)–C(20) = 113(3), O(11)–C(18)–O(12) = 112(2).

We believe that the ligand L is the result of cycloaddition of the 1,1,1-trifluoro-2,2-propanediol to the hfacac ligand promoted by the metal complex and the amino groups on the bdmapH

---

[1] (a) Bidell, W.; Döring, J.; Bosch, H. W.; Hund, H. U.; Plappert, E.; Berke, H. *Inorg. Chem.* **1993**, *32*, 502. (b) Miele, P.; Foulon, J. D.; Hounanian, N.; Cot, L. *J. Chem. Soc., Chem. Commun.* **1993**, 29. (c) Bradley, D. C.; Hasan, M.; Hursthouse, M. B.; Motevalli, M.; Khan, O. F. Z.; Pritchard, R. G.; Williams, J. O. *J. Chem. Soc., Chem. Commun.* **1992**, 575. (d) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R.; Martin, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 1524. (e) Methrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketones and Applied Derivatives*; Academic Press: New York, 1978. (f) Fackler, J. P., Jr. *Prog. Inorg. Chem.* **1966**, *7*, 362.

[2] Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J. C. *Polyhedron* **1990**, *9*, 1305.

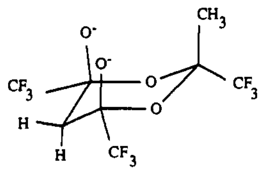
[3] March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985.

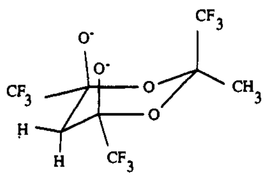
[4] Wang, S. Unpublished results.

[5] Crystal data: $C_{34}H_{43}LnCuF_{24}O_{12}N_4$, monoclinic, space group *Cc*; Ln = Y, M_r = 1308.2, a = 18.218(4) Å, b = 18.316(7) Å, c = 15.706(3) Å, β = 94.86(2)°, V = 5222(3) Å^3, Z = 4; Ln = Pr, M_r = 1360.2, a = 18.205(5) Å, b = 18.350(6) Å, c = 15.924(4) Å, β = 94.96(2)°, V = 5299(2) Å^3, Z = 4; D_{calc} = 1.72 g cm^{-3}. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV and 35 mA. The structure solution and refinements for compound **1b** were carried out by using the TEXSAN software program package on a VAX workstation, Model 3520. Systematic absences agree with both *Cc* and *C2/c* space groups. On the basis of the density of the crystal and the asymmetric nature of the molecule, the space group *Cc* was chosen. The correctness of this choice was confirmed by the successful solution and refinement of the structure. The structure was solved by direct methods (MITHRIL). The positions of hydrogen atoms were calculated and their contributions were included in the structural factor calculations. Convergence to final R values of R = 0.068 and R_w = 0.049 was achieved by using 2768 reflections [$F^2 \geq 3\sigma(F^2)$] and 341 parameters. Anal. Calcd for **1a**: C, 31.21; H, 3.31; N, 4.28. Found: C, 31.25; H, 3.14; N, 4.29. Calcd for **1b**: C, 30.02; H, 3.19; N, 4.12. Found: C, 30.89; H, 3.09; N, 3.81.

[6] Wang, S. *Inorg. Chem.* **1991**, *30*, 2252.

0020-1669/93/1332-4992$04.00/0



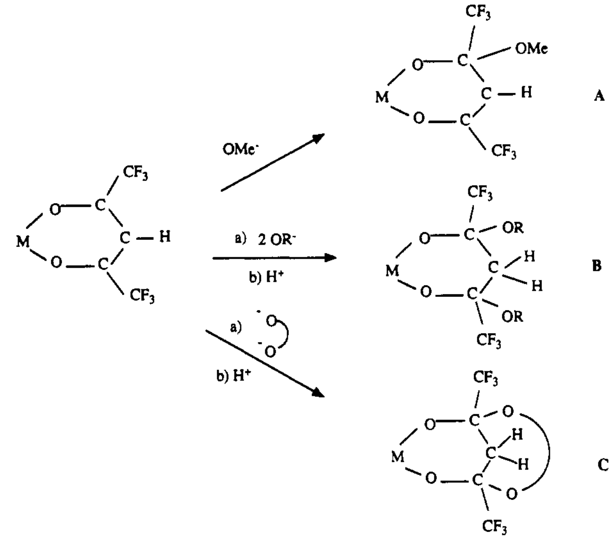


ligand. The 1,1,1-trifluoro-2,2-propanediol is the hyration product[7] of the trifluoroacetone which was produced along with the trifluoroacetate ligand by the retro-Claisen condensation reactions of the hexafluoroacetylacetone induced probably by the Lewis base bdmapH or methoxy ligand and the trace amount of H_2O from the reagents (eq 1). In fact we have observed that, in the absence of metal complexes, the addition of tetramethylpropanediamine (tmpda) to the THF solution of hexafluoroacetylacetone caused nearly quantitatively decomposition of the hfacacH molecule and the $[tmpdaH_2][O_2CCF_3]_2$ salt was isolated quantitatively. The trifluoroacetate ligand produced in the synthesis of compound **1** was trapped by the Cu(II) center to form a complex while the 1,1,1-trifluoroacetone was captured by the hfacac ligand on the Ln^{III} center to form a part of the L ligand. Based on this idea, the original synthesis was modified by introducing one equivalent of trifluoroacetone, one equivalent of trifluoroacetic acid, and one equivalent of H_2O to the reaction mixture. The crystals of compound **1** were isolated readily in about 30% yield from the modified reaction (eq 2).

$$Cu(OCH_3)_2 + Ln(hfacac)_3 + 2bdmapH + HO_2CCF_3 + CH_3C(OH)_2CF_3 \rightarrow CuLn(bdmapH)_2(hfacac)_2(O_2CCF_3)L + 2\,CH_3OH \quad (2)$$

The ligand L can be considered as a derivative of 1,3-dioxane-4,6-diol. It has a chair conformation with 4,6-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-position are disordered with 50% occupancy for both *a* and *e* positions. 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.[8] In contrast, 1,3-dioxane-4,6-diol compounds are very rare due to their tendency to dissociate back to β-diketone and the corresponding diol. To our knowledge, 1,3-dioxane-4,6-diols with or without substituents are previously unknown. Although the trifluoromethyl groups on the ligand L could contribute to the stability of this ligand, the metal centers also appear 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. Attempts 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.[9] A template–condensation process has been proposed for such reactions.[9a] The $CF_3C(OH)_2CH_3$ condensation reaction with the hfacac ligand described here may have proceeded by a similar process. The Cu(II) center may have played an important role because the L ligand was not observed when only yttrium or lanthanides complexes were employed in the synthesis. The details of the formation mechanism for L, however, has not yet been fully understood. The amino groups on the bdmap ligand appear to function as Lewis bases which remove the protons on the diol, thereby increasing its nucleophilicity. Crystallographic data seem to support this. In compound **1**, the bdmapH ligand has a zwitterion form with one of the amino groups being protonated. The protonated amino groups form hydrogen bonds with the two oxygen atoms of the L ligand as evidenced by the N(2)...O(9) distance of 2.70(3) Å and the N(4)...O(10) distance of 2.66(3) Å. A similar zwitterion form of the bdmapH ligand has been observed in the dinuclear complex[10] $Cu^{II}_2(bdmapH)_2Cl_4$.

Although nucleophilic addition reactions of alkoxy groups to fluorinated acetylacetonato ligands are not totally unexpected, the information on this type of reactions are surprisingly limited. The hfacac ligand in a cobalt(III) complex has been reported to undergo a reversible-addition reaction with a methoxy ligand and the single-addition product A has been identified.[11] The double-addition reaction B by alkoxy ligands and the cycloaddition reaction C are previously unknown, although the double-addition reaction by hydroxy ligands to β-diketones has been well established.[12] Several heterobimetallic Cu(II)–Ln(III) complexes have been claimed to be dinuclear species.[13] However, the solid-state structures of these previously reported compounds have not been established by X-ray diffraction analysis. A research effort to understand the formation mechanism and magnetic properties of these compounds has been undertaken by our group.



Acknowledgment. We thank Professor Christopher J. Willis for his valuable discussions and the NSERC of Canada for financial support.

Supplementary Material Available: Tables of atomic coordinates, crystallographic data, thermal parameters, bond lengths and angles and text giving the details of the crystallographic analysis (16 pages). Ordering information is given on any current masthead page.

---

(7) Guthrie, J. P. *Can. J. Chem.* **1975**, *53*, 898.

(8) (a) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*, 2nd ed.; Academic Press: New York, 1989; Vol. III. (b) *Heterocyclic Compounds*; Elderfield, R. C., Ed.; John Wiley & Sons: New York, 1957; Vol. 6. (c) Meskens, F. A. J. *Synthesis* **1981**, 501. (d) Gambaryan, N. P.; Rokhlin, E. M.; Zeifman, YU., V.; Chen, C. Y.; Knunyants, I. L., *Angew. Chem., Int. Ed. Engl.*, **1966**, *5*, 947.

(9) (a) Bradford, P.; Hynes, R. C.; Payne, N. C.; Willis, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 2647. (b) Modinos, A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2134.

(10) Zheng, J. C.; Rousseau, R. J.; Wang, S. *Inorg. Chem.* **1992**, *31*, 106.

(11) (a) Kitamura, Y.; Leipoldt, J. G.; Roodt, A. *Inorg. Chim. Acta* **1988**, *149*, 125. (b) Aygen, S.; Paulus, E. F.; Kitamura, Y.; Eldik, R., *Inorg. Chem.* **1987**, *26*, 769.

(12) Bouwman, E.; Huffman, J. C.; Lobkovsky, E. B.; Christou, G.; Tsai, H. L.; Hendrickson, D. N. *Inorg. Chem.*, **1992**, *31*, 4436 and references therein.

(13) (a) Matsumoto, N.; Sakamoto, M.; Tamaki, H.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 853. (b) Sakamoto, M.; Takagi, M.; Ishimori, T.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1613.