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Synthesis and Characterization of a Novel Gd(III)-Cu(II) Dinuclear Adduct

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Abstract

Two novel Gd(III)-Cu(II) dinuclear complexes have been prepared by the acid-base reaction between Gd(hfa)₃ and Cu(2,2-oxomac) (**1**, Cu(2,2-oxomac)Gd(hfa)₃) and between Gd(hfa)₃ and Cu(3,2-oxomac) (**2**, Cu(3,2-oxomac)Gd(hfa)₃). These complexes have been characterized by elemental analysis and infrared spectroscopy. The structure of **1** has been determined by X-ray diffraction. The copper atom is square pyramidal, bound to the four planar nitrogen atoms of the macrocycle and weakly bound to the oxygen atom of a dimethylformamide (dmf) molecule. The gadolinium atom is at the center of a tricapped trigonal prism. The nine-coordinate gadolinium atom is bound to six oxygen atoms of three hfa ligands, the two oxamide oxygen atoms of the copper macrocycle, and one oxygen atom of a second coordinated dmf molecule. Unsymmetric binding of the copper macrocycle to gadolinium leads to a distortion in the bridging atoms not observed in reactions of the copper macrocycles with transition metal hfa's.

Graphical abstract—The reaction of Cu(2,2-oxomac) with Gd(hfa)₃ yields a Gd(III)-Cu(II) dinuclear complex with an oxamide bridge between copper(II) and gadolinium(III). The gadolinium atom adopts a tricapped trigonal prismatic geometry.

Keywords

tricapped trigonal prismatic; gadolinium; dinuclear

Complexes **1** (Cu(2,2-oxomac)Gd(hfa)₃) and **2** (Cu(3,2-oxomac)Gd(hfa)₃) were prepared as part of a study investigating the magnetic properties of heterodinuclear complexes of f and d block metals. It has been predicted by Gatteschi^[1] that the isolated Gd(III)-Cu(II) interaction will be ferromagnetic regardless of structural considerations. Most of the dinuclear complexes for which both structural and magnetic analyses have been reported thus far contain Gd(III) coupled to Cu(II) via phenolato, acetato or acetonato donors and support the prediction of ferromagnetism.^[2] In earlier work in this lab, two phenolato bridged examples of the couple, Cuprpen and Niprpen adducts with Gd(hfa)₃, were structurally characterized; and the Gd(III)-

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Cu(II) dinuclear was found to exhibit a ferromagnetic interaction as well.^[3] However, Costes et al. have reported the synthesis of an antiferromagnetically coupled Gd(III)-Cu(II) dinuclear complex in which Gd(III) and Cu(II) are unsymmetrically bridged by a phenolate O and an oximato (N-O) group.^[4]

The reactions described in this work are part of an effort to expand the type of bridging ligand used to link Gd(III) and Cu(II). In previous work we demonstrated the effectiveness of Cu(2,2-oxomac)^[5] and Cu(3,2-oxomac)^[6] (see figure 1) as dinucleating ligands by the preparation of adducts between these complexes and M(hfa)₂ (M = Cu or Ni) in which two oxamide oxygen atoms on adjacent carbon atoms of the macrocycles serve as linkages between Cu(II) and M (II). The affinity of gadolinium for oxygen donors suggested the reaction of Gd(hfa)₃ with the copper macrocycles to yield similar dinuclear adducts with the desired Gd(III)-Cu(II) linkage.

The starting copper macrocycles, Cu(2,2-oxomac)^[7] and Cu(3,2-oxomac)^[7] and Gd(hfa)₃·2H₂O^[8] were synthesized as reported previously. Compounds **1** and **2** were prepared by adding one equivalent of Gd(hfa)₃·2H₂O to a solution of the copper macrocycle followed by recrystallization of the resulting precipitate. To obtain **1** a solution of Gd(hfa)₃·2H₂O (0.051 mmol, 0.042g) in about 10mL methanol was added to 65 mL of a methanolic solution of Cu(2,2-oxomac) (0.051 mmol, 0.019g). As the solution concentrated, a brown powder precipitated. The powder was recrystallized from a minimum volume of dimethylformamide to give red crystals suitable for X-ray analysis (0.028 mmol, 0.032g, 55% yield). (Found: C, 35.70%; H, 2.35%; N, 5.93%. C₃₃H₁₇CuF₁₈GdN₄O₈ · 1.5DMF requires C, 35.47%; H, 2.18%; N, 6.07%.) For compound **2**, Cu(3,2 oxomac) (0.065 mmol, 0.026g) was dissolved in 20–30 mL chloroform with heating. Gd(hfa)₃·2H₂O (0.066 mmol, 0.054g) in 5–10 mL chloroform was added. There was an immediate color change from the dark olive green color of Cu(3,2-oxomac) to a bright green followed by precipitation of a bright green powder (0.079g, quantitative conversion). (Found: C, 31.58%; H, 1.13%; N, 4.16%. C₃₄H₁₉CuF₁₈GdN₄O₈ · 1.5CHCl₃ requires C, 31.54%; H, 1.54%; N, 4.15%.) Recrystallization of the solid from DMF did not produce crystals suitable for X-ray diffraction.

For compound **1** a single crystal crystallographic experiment was carried out on an Enraf-Nonius FAST area detector diffractometer at 130 K by methods and procedures for small molecules standard in this lab.^[9] A summary of determined parameters is given.^[10]

Compounds **1** and **2** were synthesized by reaction of the copper macrocycles with Gd(hfa)₃. Elemental analyses of **1** and **2** were consistent with their formulation as Cu(2,2-oxomac)Gd(hfa)₃ and Cu(3,2-oxomac)Gd(hfa)₃, respectively. In addition, formation of the dinuclear adducts was apparent by comparing the infrared spectra of **1** and **2** with that of the starting materials. The IR spectra of both products are largely a combination of the IR spectra of starting materials, with some shifting of bands in the carbonyl and imine regions, which is expected upon complexation. For both **1** and **2** similar bands attributable to the trifluoromethyl groups of Gd(hfa)₃ dominate the IR spectra at 1254, 1205 and 1145 cm⁻¹ for **1** and at 1257, 1206, and 1146 cm⁻¹ for **2**. Other significant absorptions in the IR spectrum of **1** are 1659 (s), 1609 (m), 1523 (m), and 1506cm⁻¹(m). For **2** these are 1654 (s), 1608 (m), 1531 (m), and 1504 cm⁻¹(m). For comparison, the parent copper macrocycles exhibit two strong bands in this region at 1646 and 1619 cm⁻¹ for Cu(2,2-oxomac) and at 1650 and 1632 cm⁻¹ for Cu(3,2-oxomac). Gd(hfa)₃ exhibits its strongest absorptions at 1650 and 1619 cm⁻¹ in this region. Mass spectral analysis of this class of adduct reveals the presence of both starting materials.

Figure 2 shows the structure of **1**. The dmf molecule which is bound to Cu(II) has been omitted for clarity. The gadolinium atom is nine-coordinate, bound to O(1), O(2), O(3), O(4), O(5) and O(6) of the hfa ligands, O(7) and O(8), the two oxamide oxygen atoms of Cu(2,2 oxomac), and O(9) of a dimethylformamide molecule. The coordination geometry of gadolinium is a

tricapped trigonal prism with capping oxygen atoms in the center of the three rectangular faces as shown in figure 3. The average Gd–O distance is 2.431 Å. The average bite angle of the hfa ligands is 70.67°. The trigonal faces of the tricapped trigonal prism are defined by O(2)–O(5)–O(6) and O(7)–O(9)–O(4) with O(2) eclipsing O(7), O(5) eclipsing O(9), and O(6) eclipsing O(4). Bond angles between gadolinium and two eclipsing oxygen atoms of opposite trigonal planes are 80.66° for O(2)–Gd–O(7), 99.36° for O(5)–Gd–O(9), and 89.80° for O(6)–Gd–O(4). The oxygen atoms which cap the three rectangular faces are approximately trigonal planar with an average angle between capping oxygen atoms and gadolinium of 119.97°. Coordination of the two oxamide oxygen atoms of the copper chelate to the gadolinium atom is not symmetric. One of the oxygen atoms forms a vertex of the trigonal prism in the gadolinium coordination geometry and the other caps a rectangular face. These two Gd–O distances are 2.399 Å and 2.429 Å, respectively, and the bite angle is 65.39°. The analogous bite angle in the Ni(hfa)₂ adduct is 78.9°. Comparison of these two values should be done cautiously because of the differences in the basic coordination geometries and metal oxygen bond distances.

The copper atom is five-coordinate, bound to its original N₄ donor set with a long bond to a dmf oxygen atom of 2.471 Å and displaced from the plane defined by N(1), N(2), N(3), and N(4) by 0.213 Å. By contrast, in Cu(2,2-oxomac), the copper coordination environment is square planar with a displacement of only 0.003 Å from the N(1)–N(4) plane.^[5]

Unsymmetric binding of the two oxamide oxygen atoms leads to distortion of the copper chelate as compared to what is found in the dinuclear adduct between Cu(2,2-oxomac) and Ni(hfa)₃.^[5] An examination of the angle between the plane defined by the four nitrogen donor atoms of the copper macrocycle (the N₄ plane) and the plane defined by Cu–N(1)–C(16)–C(33)–N(4) (the “oxamide” plane) reveals the distortion. For the other dinuclear complexes of Cu(2,2-oxomac) and Cu(3,2-oxomac) with M(hfa)₂ structurally characterized in this lab, a relatively planar arrangement of the two metal atoms and bridging ligands has been observed. In the parent macrocycle Cu(2,2-oxomac) the interplanar angle between the N₄ and the “oxamide” planes is only 1.9°. Upon binding to Ni(hfa)₂, the interplanar angle for the analogous sets of atoms is even smaller, 0.1°, affording a nearly planar arrangement of the two metals and their bridging ligands. The same effect is observed for the dinuclear complex formed by the reaction of Cu(3,2-oxomac) with Cu(hfa)₂.^[6] For Cu(2,2-oxomac)Gd(hfa)₃, however, a gross distortion is observed. The angle between the N₄ and the “oxamide” planes is increased to 13.4°, effectively “bending” the oxamide bridge out of the N₄ plane. One of the oxamide oxygen atoms, O(7), is nearly coplanar with the “oxamide” plane (a 0.046 Å displacement), but the other, O(8), is displaced 0.232 Å out of the plane. The gadolinium atom is displaced from the “oxamide” plane by 0.442 Å. By contrast, the nickel atom in the Cu(2,2-oxomac)Ni(hfa)₂ is coplanar with the “oxamide” plane.

The gadolinium and copper atoms are separated by 5.699 Å and bridged by the N1–C16–O7 and N4–C33–O8 pathways. Upon binding to gadolinium, the N(1)–C(16) and N(4)–C(33) bonds shorten from an average of 1.360 Å in the mononuclear Cu(2,2-oxomac) to an average of 1.325 Å in the dinuclear complex. Also upon binding to gadolinium, the C(16)–O(7) and C(33)–O(8) distances of the oxamide lengthen from an average of 1.228 Å to 1.253 Å. The same effect was observed in the analogous complex of Cu(2,2-oxomac) with Ni(hfa)₂.^[5] This is consistent with an increase in N=C–O[–] and a decrease in [–]N–C=O character for the oxamide moiety in Cu(2,2-oxomac) on binding to an external metal atom.

The magnetism of compound **2** is similar to that of the previously reported adduct of Gd(hfa)₃ with Cuprpn.^[3] and exhibits a low temperature moment of 8.6 B.M. The magnetic behavior of **1** did not fit the expected Heisenberg exchange coupled model for a S=7/2, S=1/2 system. Further magneto-structural discussion is unwarranted until other data including the

structure of Cu(3,2-oxomac)Gd(hfa)₃, and the structure and magnetism of Ni(2,2-oxomac)Gd(hfa)₃ (diamagnetic blank) is available.

The reaction of Gd(hfa)₃·2H₂O with copper macrocycles containing adjacent oxamide O atoms that can bind to a second metal has produced two novel dinuclear adducts in which Gd(III) is linked to Cu(II) via an oxamido bridge. This work extends the series of M(hfa)_n adducts with M(2,2-oxomac) and M(3,2-oxomac) complexes and provides a new route to the synthesis of Gd(III)-Cu(II) dinuclears for magnetic study and provides a novel example of a tricapped trigonal prismatic geometry in a dinuclear adduct with a transition metal complex.

Supplementary material

Crystallographic data from the structural analysis of **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No.168423, the Editor, and are available from the author.

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10. Crystallographic data for compound **1**: Crystal dimensions = 0.18 × 0.12 × 0.08 mm, formula C₃₉H₃₁CuF₁₈GdN₆O₁₀, triclinic, space group P1̄ with a = 11.2751(7), b = 14.2201(19), c = 16.372(2) Å, α = 96.267(19)°, β = 109.903(5)°, γ = 101.305(10)°, V = 2375.8(5) Å³, Z = 2, D_c = 1.826 Mg/m³, F(000) = 1284, λ = 0.71073 Å, T = 130(2) K. A red block-shaped crystal of **1** was used for data collection, which had a refined effective mosaic spread of 0.874°. A total of 23152 reflections were collected up to 29.97° for theta angle, of which 12251 were unique and intensities of 10656 unique reflections were larger than 2.0σ(I). All reflections were reduced using Lorentz-polarization factors. The structure was solved in the space group P1̄ by direct methods from the SHELXS-86 program^[9b] A group of fluorine atoms [F(7)-F(9)] was found disordered on two sets of positions that were related by a rotation along the C-C bond. Another group [F(13)-F(15)] was also suggested by large ADP Max/Min ratios to have a similar rotational disorder; however, attempts to refine a working disorder model failed. After all these non-hydrogen atoms were found anisotropically, most of the hydrogen atoms were located by the difference Fourier synthesis. However, in the least-squares refinement, all hydrogen atoms were put in idealized positions and refined with riding models (C-H = 0.95 Å for R₂CH, 0.99 Å for R₂CH₂, 0.98 Å for RCH₃). Apart from averaging large numbers of redundant and equivalent data collected with different diffractometer settings, an empirical absorption correction was made at this stage with the program DIFFAST, an adapted version of DIFABS^[9c] for FAST data sets, which improved satisfactorily merging R value for equivalent data and the final convergence R values. The structure was refined against F² by the SHELXL-93 program^[9b] The refinement converged to a final value of R₁ = 0.0535 and wR₂ = 0.1274 for observed unique reflections (I ≥ 2.0σ(I)) and R₁ = 0.0646 and wR₂ = 0.1348 for all unique reflections including those

with negative intensities. The weighted R-factors, wR, are based on F^2 and conventional R-factors, R, on F, with F set to zero for negative intensities. All reflections, including those with negative intensities, were included in the refinement and the $I \geq 2.0\sigma(I)$ criterion was used only for calculating R_1 . The maximum and minimum residual electron densities on the final difference Fourier map were $2.085 \text{ e/\AA}^3$ and $-1.826 \text{ e/\AA}^3$, respectively, and featureless.

Cu(2,2-oxomac)

Cu(3,2-oxomac)

Figure 1.
Line drawings of Cu(2,2-oxomac) and Cu(3,2-oxomac).

Figure 2.

ORTEP of $\text{Cu}(2,2\text{-oxomac})\text{Gd}(\text{hfa})_3$ (1). The dmf bound to Cu(II) has been omitted for clarity. Selected bond distances ($\text{\AA}$) and angles ($^\circ$): Gd-O(1), 2.476(3); Gd-O(2), 2.469(3); Gd-O(3), 2.464(3); Gd-O(4), 2.440(3); Gd-O(5), 2.399(3); Gd-O(6), 2.384(3); Gd-O(7), 2.399(3); Gd-O(8), 2.429(3); Gd-O(9), 2.419(3); Cu-N(1), 1.950(3); Cu-N(2), 1.947(4); Cu-N(3), 1.941(4); Cu-N(4), 1.952(3); O(1)-Gd-O(2), 68.89(10); O(3)-Gd-O(4), 70.08(10); O(5)-Gd-O(6), 73.04(11); O(7)-Gd-O(8), 65.39(10).

Figure 3.
Tricapped trigonal prismatic arrangement of oxygen atoms coordinated to gadolinium.