SYNTHESIS, STRUCTURE, AND MAGNETISM OF HETEROBINUCLEAR COMPLEX GdCu(OTf)$_3$(bdmap)$_2$(H$_2$O) · THF
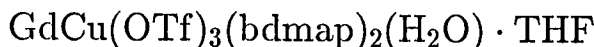
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A new heterobinuclear Gd(III)–Cu(II) complex [GdCu] = GdCu(OTf)$_3$(bdmap)$_2$(H$_2$O) · THF (OTf = SO$_3$CF$_3$) has been prepared by reaction of 1,3-bis(dimethylamino)-2-propanol (bdmapH) with Cu(OCH$_3$)$_2$ and lanthanide triflate salt Gd(OTf)$_3$ in a 2 : 1 : 1 ratio in THF. Its structure has been determined by single-crystal X-ray diffraction. [GdCu] crystallizes on an orthorhombic lattice, space group $P2_12_12_1$ with $Z = 4$ and $a = 11.023(3)$ Å, $b = 17.555(15)$ Å, $c = 20.212(7)$ Å, $V = 3911(4)$ Å^3. For 2194 independent reflections with $I > 1\sigma(I)$, full-matrix least squares refinement with anisotropic thermal parameters for Gd, Cu, S, and O converged to unweighted and weighted R factors of 0.074 and 0.085, respectively. Gd is coordinated by six O and two N. Cu is coordinated by two O and two N. Gd and Cu are bridged by two alkoxo O atoms with separation of 3.311(4) Å. The magnetic susceptibilities were measured over the temperature range 1.7–20 K at the field range 0.01–0.5 T. The data of [GdCu] at 0.05 T have been analyzed with the use of a Heisenberg spin Hamiltonian $\hat{H} = -2J\hat{S}_{\mathrm{Gd}} \cdot \hat{S}_{\mathrm{Cu}}$ giving $g = 2.046(2)$, $J = -0.039(3)$ cm^{-1}. This shows that Gd–Cu spins are coupled very weakly in the antiferromagnetic manner, though the distance between Gd(III) and Cu(II) ions is rather short.

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1. Introduction

In the last decade, several kinds of [Gd$_x$Cu$_y$] heteronuclear complexes were structurally and magnetochemically characterized, for example compounds with clusters: [Gd$_2$Cu$_2$] [1], [GdCu$_2$] [2, 3], [Gd$_2$Cu$_4$] [4], [GdCu$_3$] [5], and two-dimensional layers [Gd$_2$Cu$_3$·Cu] [6, 7]. Up to now, the observed spin–spin coupling between Gd(III) and Cu(II) is almost in the ferromagnetic manner with one exception [8]. In this paper the first structurally characterized [GdCu] binuclear complex and its magnetic properties are reported.

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2. Experimental section

2.1. Synthesis

Reactions were carried out under argon atmosphere by using standard Schlenk techniques. 1 mmol of $Cu(OCH_3)_2$ (Aldrich Chemical Co.) was dissolved in 30 ml of dry THF, and 2 mmol of 1,3-bis(dimethylamino)-2-propanol (bdmapH, Aldrich Chemical Co.) were added while stirring. After 2 hours, 1 mmol of Gd(OTf)$_3$ (obtained from Gd$_2$O$_3$ and HOTf as described previously [9, 10]) was added to the purple suspension. The mixture was stirred for 12 h at room temperature to yield a blue solution. The solution was filtered by suction and the solvent was evaporated to 5 ml. Blue crystals formed over a period of 5 d upon adding hexane.

2.2. Magnetic susceptibility measurements

Magnetic susceptibility data were collected in the temperature range of 1.7–20 K at magnetic fields ranging from 0.01–0.5 T employing the MSPS-5S SQUID magnetometer. The data were corrected for diamagnetic contributions using Pascal's constants.

2.3. X-ray structure determination

A single crystal of [GdCu] (0.15 × 0.20 × 0.33 mm^3) was used for crystal data collection on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K_α radiation in the 2θ-scan mode ($2\theta_{max} = 48°$). Lattice parameters were determined by least squares refinement of the setting angles of 25 computer-centered reflections in the range of $0.01° \leq 2\theta \leq 48.0°$. The data were empirically corrected for Lorentz polarization and absorption. The crystal belongs to the orthorhombic system, the space group being $P2_12_12_1$ as indicated by the systematic absences. The structure was solved using direct methods (NRCVAX)[11]. Hydrogen atoms were located in calculated positions (C–H = 1.08 Å). The final refinement (NRCVAX) converged to $R = 0.074$ and $R_w = 0.085$ by using 2194 independent reflections with $I > 1\sigma(I)$. The maximum residual peak in the last difference Fourier map is 0.94 $e\text{Å}^{-3}$.

3. Results and discussion

3.1. Crystal and molecular structure

The molecular structure of [GdCu] is shown in Fig. 1. Selected bond lengths and bond angles are given in Table. Gd is linked with Cu through two alkoxo O atoms of bdmap with a Gd–Cu separation of 3.311(4) Å, which is the second shortest Gd–Cu distance found in all reported [Gd$_x$Cu$_y$] complexes [5, 12, 13]. Gd is eightfold coordinated in an irregular manner by two alkoxo O atoms, three O atoms of OTf anions, one O atom of water, and two N atoms of two bdmap. Cu is fourfold coordinated by two N and two O atoms of two bdmap, forming a slightly D_{2d} distorted square (distances to the plane: O1, 0.15(3); O2, −0.13(3); N1, −0.13(3); N2, 0.22(4) Å). O12 and O33 of two OTf anions look like two axial
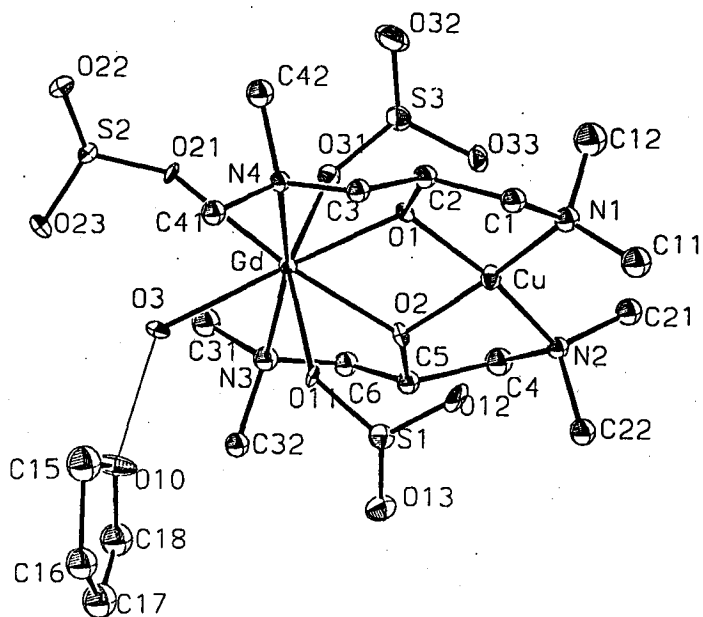
Fig. 1. ORTEP view of the complex [GdCu] and labeling scheme. Fluorine and carbon atoms of the triflate anions are omitted.
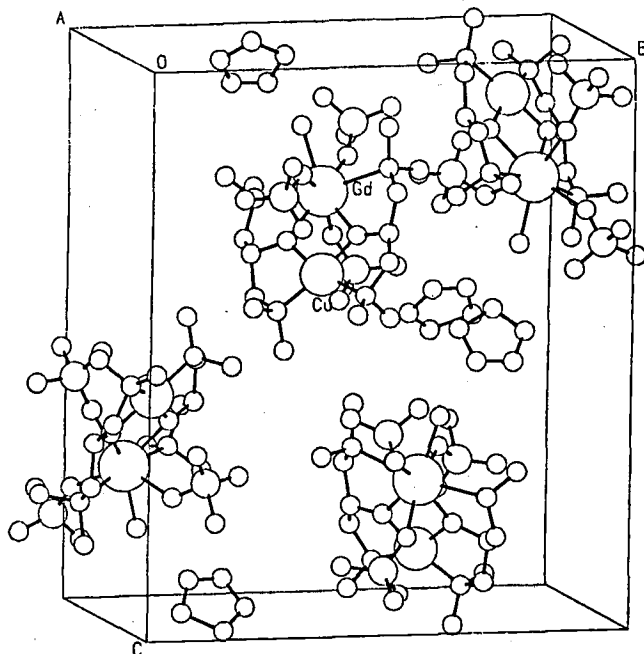

Fig. 2. Schematic view of the unit cell of [GdCu].

Selected bond lengths (Å) and bond angles (deg) for [GdCu].

Bond	Lengths	Bond	Lengths	Bond	Lengths
Gd–Cu	3.311(4)	Cu–O2	1.892(19)	C1–C2	1.58(6)
Gd–O1	2.215(20)	Cu–N1	2.02(3)	C3–C2	1.54(5)
Gd–O2	2.278(20)	Cu–N2	2.06(3)	O1–C2	1.36(4)
Gd–O3	2.418(22)	C4–C5	1.57(5)	O2–C5	1.45(4)
Gd–O11	2.411(22)	C5–C6	1.38(6)	S1–O11	1.476(22)
Gd–O21	2.477(18)	N1–C1	1.51(5)	S2–O21	1.402(19)
Gd–O31	2.42(3)	N2–C4	1.46(6)	S3–O31	1.47(3)
Gd–N3	2.62(3)	N3–C6	1.50(5)	O10–C15	1.38(7)
Gd–N4	2.71(3)	N4–C3	1.45(5)	O10–C18	1.29(6)
Cu–O1	1.914(21)				

Bond	Angles	Bond	Angles	Bond	Angles
O1–Gd–O2	67.2(7)	O11–Gd–O2	74.6(7)	O2–Cu–N2	83.5(10)
O1–Gd–O31	77.2(9)	O11–Gd–O3	71.2(7)	N1–Cu–N2	110.2(13)
O1–Gd–O11	85.6(8)	O11–Gd–N4	79.1(8)	Gd–O1–Cu	106.4(8)
O1–Gd–N4	63.9(7)	O3–Gd–O21	68.9(7)	Gd–O2–Cu	104.7(9)
O31–Gd–O2	79.5(8)	O3–Gd–N3	80.3(9)	Gd–O1–C2	131.7(19)
O21–Gd–N4	81.2(8)	O3–Gd–N4	87.9(7)	Cu–O1–C2	113.9(20)
N3–Gd–N4	168.1(8)	O2–Gd–N3	63.8(8)	Gd–O2–C5	127.6(18)
O31–Gd–O21	71.3(8)	O1–Cu–O2	81.6(9)	Cu–O2–C5	121.9(17)
O31–Gd–N3	77.0(9)	O1–Cu–N1	86.5(11)		

coordinated atoms towards Cu(II) with Cu–O distances 2.79(2) and 2.78(2) Å, respectively. The angle of O12–Cu–O33 is 164°. The atoms Gd, Cu, O1, O2 form a perfect plane. O10 of THF is connected with O3 by a hydrogen bond, the distance between O10 and O3 is 2.57 Å. Four binuclear units are packed in the unit cell shown in Fig. 2. Between binuclear units, the minimum separations for Gd–Gd, Gd–Cu, and Cu–Cu are 9.598, 8.264, and 8.757 Å, respectively.

3.2. Magnetic properties

The magnetic susceptibility data (at 0.05 T) were fitted to the Curie–Weiss law ($\chi_m = C/(T - \theta)$). Good agreement was found with $C = 8.63(1)$ cm^3 K mol^{-1} and $\theta = -0.056(4)$ K. The small θ value indicates very weak antiferromagnetic exchange coupling between the metal ions. The magnetic moment expected for non-interacting [GdCu] units and $g = 2$ is 8.12 μ_B, while the observed effective magnetic moment μ_{eff} is in the range from 8.18 μ_B (1.7 K) to 8.23 μ_B (20 K) with a maximum value of 8.30 μ_B at 8 K (see Fig. 3a).

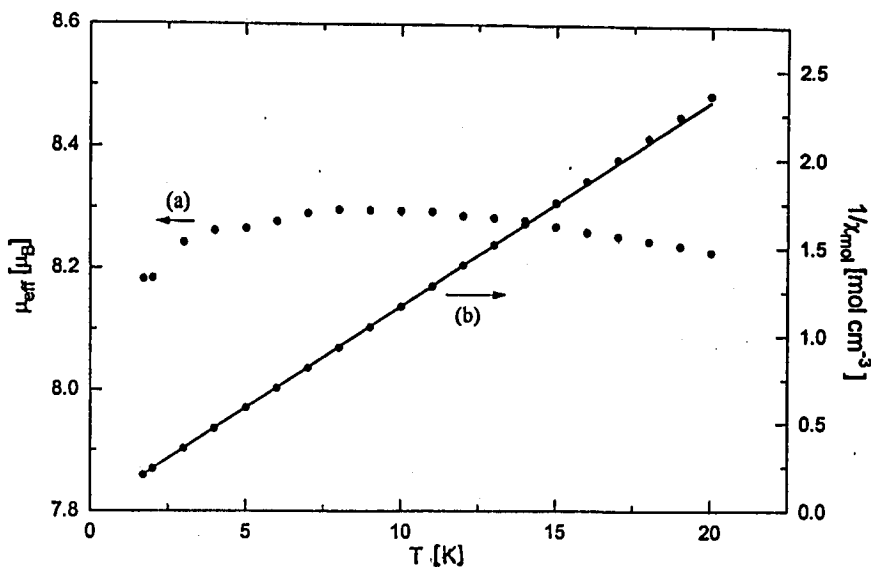The X-ray structure analysis has shown that all separations between Gd–Gd,

Fig. 3. Temperature dependence of μ_{eff} (a) and $1/\chi_m$ (b) for [GdCu](• exp., — calc.).

Gd–Cu, and Cu–Cu between [GdCu] units are longer than 8 Å. Thus, intermolecular interactions can be neglected. The spin Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Gd}} \cdot \hat{S}_{\text{Cu}}$ has been used to derive the susceptibility equation [14, 15]:

$$\chi_m = (4Ng^2\beta^2/kT)[15 + 7\exp(-8J/kT)]/[9 + 7\exp(-8J/kT)].$$

The magnetic susceptibility data of [GdCu] at 0.05 T have been fitted using this equation, the best fit was obtained with $g = 2.046(2)$, $J = -0.039(3)$ cm^{-1} (see Fig. 3b). The very small negative value of J shows a very weak antiferromagnetic coupling between Gd(III) and Cu(II) ions consistent with the negative θ value. It is worth noting that in the previously investigated [Gd$_x$Cu$_y$] complexes, the bridging ligands contain a conjugated system. In the title compound [GdCu], however, the bridging system has exclusively σ bonds. In spite of the rather short Gd–Cu separation, the magnitude of $|J|$ for [GdCu] is the smallest one observed so far. This indicates that the nature of bridging ligands is an important factor controlling the magnitude of the spin–spin coupling, in addition to the distance between metal ions and the angle in bridging network. Detailed magnetochemical investigations into [GdCu] and isostructural [NdCu] with respect to the temperature and field dependences of the susceptibility are in progress.

Acknowledgment

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