Synthesis, Crystal Structure, and Magnetic Properties of the Mixed-Ligand Complex [$Gd(CF_3CO_2)_3(phen)_2(H_2O)$]

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Introduction

The complexation of gadolinium(III) ions with multidentate ligands with O- and N-donors, particularly polyaminocarboxylates, has received great attention because of its relevance in biomedical applications as magnetic resonance imaging (MRI) agents.[1−8] However, structurally characterized gadolinium complexes containing separate O- and N-donor ligands of low denticity remain rather unexplored likely because of the weak stereochemical preferences of the lanthanide ions. A search in the Cambridge Crystallographic Database[9] revealed one gadolinium trichloroacetate with 1,10-phenanthroline as a neutral ligand, namely, dimeric [$Gd_2(CCl_3CO_2)_6(phen)_2(EtOH)_2$]. The structure shows two eight-coordinate GdN_2O_6 cores bridged by four trichloroacetates in the classical η^1:η^1:μ_2 way.[10] The dimeric nature of the acetate derivative [$Gd_2(CH_3CO_2)_6(phen)_2(H_2O)_2$] was also established, although no quantitative details of the structure were given. This compound is isostructural with its Ce(III) analogue and contains two nine-coordinate GdN_2O_7 cores with the Gd(III) ions bridged by four acetato groups, two in the classical η^1:η^1:μ_2 and two in the η^2:η^1:μ_2 fashion. In the latter two compounds evidence was found for weak intermolecular magnetic interactions between the 4f cations.[11] In addition, a crystal structure determination has been reported for the gadolinium nitrate derivative [$Gd(phen)_2(NO_3)_3$], a mononuclear compound with a 10-coordinate GdN_4O_6 core.[12]

In view of these results it seemed interesting to incorporate the highly electron-withdrawing CF_3CO_2 anionic ligand in the replacement of CCl_3CO_2 and CH_3CO_2 and analyze its influence on the nature of the resulting complex. Herein we report on the preparation, the single-crystal X-ray structure, and the magnetic behavior of the novel mononuclear mixed-ligand complex [$Gd(CF_3CO_2)_3(phen)_2(H_2O)$].

Experimental Section

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA 1108 instrument. Infrared spectra were recorded on a Nicolet FT-IR 510 P spectrophotometer using the KBr pellet technique. Thermal analysis was performed on a Shimadzu DTG 50 thermal analyzer, under air flow (40 L/min) at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer. Temperature-dependent magnetic susceptibilities of solid samples were recorded on a SHE 906 SQUID susceptometer in the range 5−300 K with an applied field of 0.5 T. Pascal's constants were used to estimate the correction for the underlying diamagnetism of the sample. EPR spectra on a polycrystalline sample were obtained with a 9.8 GHz Bruker spectrometer using a Bruker rectangular cavity with 100 kHz field modulation.

Synthesis of [$Gd(CF_3CO_2)_3(phen)_2(H_2O)$]. Trifluoroacetic acid (0.70 g, 6.0 mmol) was added slowly to 10 cm^3 of an aqueous suspension of Gd_2O_3 (0.35 g, 1 mmol) kept in an ice bath. The reaction mixture was allowed to warm to room temperature and maintained with stirring overnight. A methanolic solution of phen·H_2O (0.80 g, 4 mmol) was added with stirring, and the resulting solution was filtered and allowed to stand at room temperature in a stoppered flask for 3 weeks. A colorless solid separated, which was washed with a small amount of ice water and dried in air. Yield: 1.20 g, 70%. Anal. Calcd for $C_{30}H_{18}N_4F_9O_7Gd$: C, 41.16; H, 2.07; N, 6.40. Found: C, 41.25; H, 2.10; N, 6.30. IR (KBr disk, cm^{-1}): 3386m,br $\nu_{(OH)}$, 3079w, 1698vs ($\nu_{CO2asym}$), 1628sh, 1592s (phen), 1578m, 1520s, 1426vs (ν_{CO2sym}), 1347m 1208vs and 1132vs(ν_{CF3}), 1106s, 864s (phen), 847, 797s, 731vs (phen), 723vs, 639m, 604w, 272w. Thermogravimetric analysis shows that one water molecule per formula weight (2.06%) is lost in the range 60−80 °C. The mass of the final product at 490 °C corresponds to the complete combustion of the compound to cubic Gd_2O_3 as shown in the X-ray powder diffraction pattern.[13]

X-ray Crystallography. A suitable crystal of the complex, a colorless block with approximate dimensions of 0.56 mm × 0.36 mm × 0.28 mm, was used. Data were collected at room temperature on a Siemens R3m four-circle diffractometer using a $\theta-2\theta$ scan mode ($2° < 2\theta < 50°$). The three terminal CF_3 groups present rotational disorder around their C−C bonds. The refinement problem was circumvented by positioning an adequate number of fluorine atoms at the circular loci defined by these rotations, restrained to the condition of having

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Table 1. Crystal Data and Structure Refinement for $[Gd(CF_3CO_2)_3(phen)_2(H_2O)]$

chemical formula: $C_{30}H_{18}N_4O_7F_9Gd$	fw = 874.73
$a = 11.889(2)$ Å	space group: $P\bar{1}$ (No.2)
$b = 12.158(2)$ Å	$T = 22(1)$ °C
$c = 13.225(2)$ Å	λ(Mo Kα) = 0.710 73 Å
$\alpha = 76.69(1)°$	$\rho_{calcd} = 1.75$ g cm^{-3}
$\beta = 85.59(1)°$	$\mu = 21.1$ cm^{-1}
$\gamma = 62.90(1)°$	R1 ^{a} $[F^2 > 2\sigma(F^2)] = 0.047$
$V = 1655.2(5)$ Å^3	wR2 ^{b} $[F^2 > 2\sigma(F^2)] = 0.112$
$Z = 2$	

^{a} $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Gd(CF_3CO_2)_3(phen)_2(H_2O)]$

Gd(1)−O(1X)	2.319(3)	O(1X)−C(1X)	1.259(6)
Gd(1)−O(1U)	2.358(4)	O(2X)−C(1X)	1.236(6)
Gd(1)−O(1W)	2.414(4)	C(1X)−C(2X)	1.489(6)
Gd(1)−O(1V)	2.439(4)	O(1V)−C(1V)	1.262(6)
Gd(1)−N(1A)	2.535(4)	O(2V)−C(1V)	1.238(6)
Gd(1)−N(2B)	2.580(4)	C(1V)−C(2V)	1.486(7)
Gd(1)−N(1B)	2.613(4)	O(1U)−C(1U)	1.277(6)
Gd(1)−N(2A)	2.622(4)	O(2U)−C(1U)	1.236(7)
Gd(1)−O(2V)	2.666(5)	C(1U)−C(2U)	1.497(7)
Gd(1)−C(1V)	2.894(4)		
(O1V)−Gd(1)−O(2V)		50.51(13)	
N(1A)−Gd(1)−N(2A)		63.95(13)	
N(1B)−Gd(1)−N(2B)		63.23(13)	

occupation factors that add up to 3. This proved to be a better model than the superposition of a set of four ideal rigid CF_3CO_2 groups rotated 30° apart. The residual electron density peaks were not greater than 0.85, and the two hydrogen atoms from the coordinated water molecule were clearly seen in the latest difference Fourier maps. They were subsequently refined with no constraints, leading to a neat description of the H-bonding scheme. A summary of the crystallographic data and structure refinement is given in Table 1. Computer programs used in this study are listed in refs 14−17.

Results and Discussion

The reaction of Gd_2O_3 with trifluoroacetic acid and 1,10-phenanthroline in water led to the isolation of compound $[Gd(CF_3CO_2)_3(phen)_2(H_2O)]$. The formulation of the compound was supported by elemental analysis, IR characterization of the ionic carboxylate, of the CF_3 group, and of the characteristic bands of coordinated 1,10-phenanthroline,[18,19] and thermogravimetric analysis. A summary of crystallographic data and structure refinement is given in Table 1; selected bond distances and angles are listed in Table 2.

Crystal Structure. The molecular structure of $[Gd(CF_3CO_2)_3(phen)_2(H_2O)]$ is represented in Figure 1. The gadolinium cation binds to nine donor atoms, four of which are nitrogen atoms that belong to two 1,10-phenantroline molecules and five of which are oxygen atoms. Two of these oxygens correspond to a chelating trifluoroacetato ligand, two to monodentate trifluoroacetato ligands, and one to a water molecule. The overall geometry is best described as a distorted tricapped trigonal prism (TCTP) with the three chelates spanning in the lower hemisphere and the three monodentate ligands in the capping positions for a "hard-sphere model".[20] The carboxylic oxygens of the two monodentate trifluoroacetate ligands form short and nearly equal Gd−O bond lengths of 2.319(3) Å [Gd(1)−O(1X)] and 2.358(4) Å [Gd(1)−O(1U)]. In contrast, the less common chelating trifluoroacetate ligand shows longer and markedly asymmetric bonds, as indicated by the Gd−O distances of 2.439(4) Å [Gd(1)−O(1V)] and 2.666(5) Å [Gd(1)−O(2V)]. The C−O bond lengths are found in the range 1.262(6)−1.236(6) Å, which is between those expected for a single C−O bond (1.43−1.34 Å) and a double C═O bond (1.21−1.16 Å),[21] suggesting that the carboxylate oxygens not bonded to the gadolinium ions may be involved in hydrogen bonding with the aqua ligands (vide infra). The Gd(1)−O_{water} bond length (2.414(4) Å) is very similar to the values found in polyaminocarboxylate complexes with a water molecule in the inner coordination sphere of the Gd(III) ion.[22] The values of the Gd(1)−N bonds (average distance of 2.588(4) Å) are significantly shorter than the Gd−N distances in the eight-coordinate centers in $[Gd_2(CCl_3CO_2)_6(phen)_2(EtOH)_2]$ (average distance of 2.693(7) Å) and likely also shorter than in the nine-coordinate centers in $[Gd_2(CH_3CO_2)_6(phen)_2]$. In fact, the Ce−N bond in the isostructural $[Ce_2(CH_3CO_2)_6(phen)_2]$ is 2.679(4) Å on average, and the difference in ionic radii between Ce(III) and Gd(III) is 0.07 Å.[23]

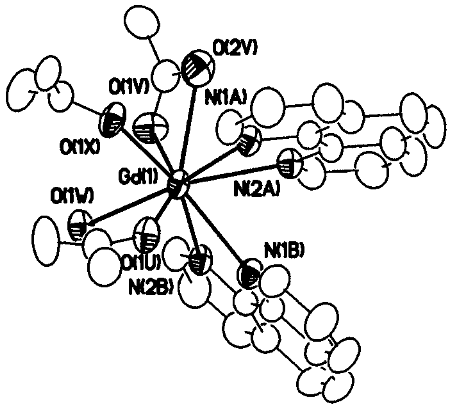

Figure 1. Diagram including the numbering scheme of the gadolinium coordination polyhedron in $[Gd(CF_3CO_2)_3(phen)_2(H_2O)]$ (40% thermal ellipsoids). For clarity, the three disordered CF_3 groups at C2U, C2V, and C2X are not shown.

The coordinated water molecule plays an important role in the association of pairs of molecular units in the solid state. One of the H atoms is involved in an intramolecular H bond with the outer carboxylate oxygen O(2U) (H(1WA)···O(2U), 2.09(9) Å; O(1W)−H(1WA)···O(2U), 149(7)°). The other H atom is involved in an intermolecular H bond to O(2X), the outer carboxylate oxygen of the centrosymmetrically related molecule (operation $2 - x, -y, 1 - z$) (H(1WB)···O(2X), 2.06(7) Å; O(1W)−H(1WB)···O(2X), 172(7)°). This set of hydrogen bonds determines a Gd−Gd separation of 7.16(1) Å (Figure 2) with the next-neighboring Gd−Gd distances at 9.06(1) Å.

Magnetic Properties and EPR Spectra. The thermal variation of the molar magnetic susceptibility of the compound in the range 5−300 K displayed in Figure 3 in the form χ_M^{-1} vs T obeys a Curie−Weiss law ($\chi_M = C/(T - \theta)$) with $C = 7.45 \pm 0.1$ emu K mol^{-1} and a negligible θ value of 0.1 ± 0.1 K.

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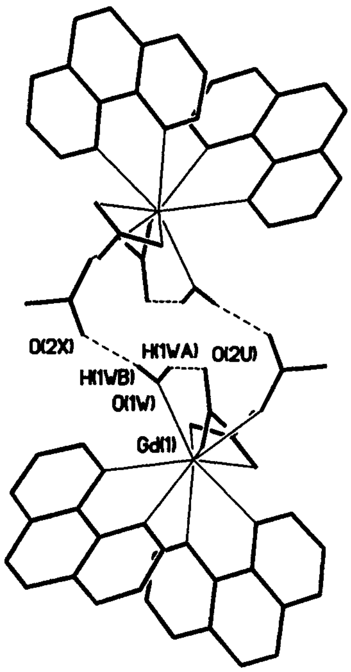

Figure 2. View of the binuclear unit showing the intra- and intermolecular H-bonding interactions. The Gd−Gd separation is equal to 7.16(1) Å.

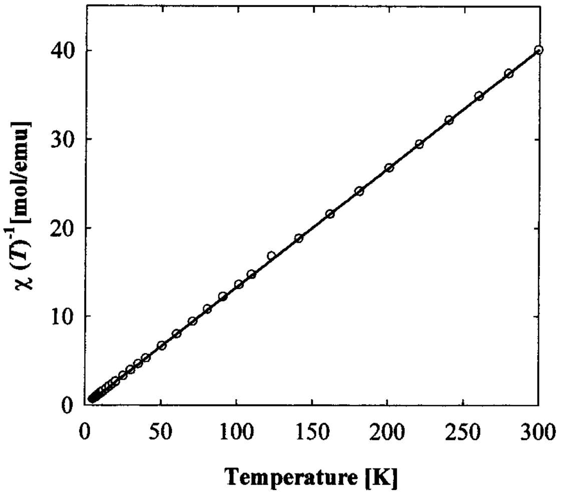

Figure 3. Molar susceptibility χ_M^{-1} vs T curve for [Gd(CF_3CO_2)$_3$-(phen)$_2$(H_2O)]. The solid line shows the best fit to the Curie−Weiss law.

The magnetic moment of 7.72 μ_B is, within error, identical to the spin-only value of 7.94 μ_B per Gd(III). These data are in agreement with the large distances between the magnetic centers of neighboring molecules. Detection of weak exchange interactions between the Gd spins would require magnetic susceptibility measurements at much lower temperatures. EPR is a technique that may overcome this problem and is particularly sensitive for determining the dimensionality of the exchange network.[24] However, it is not possible to determine the sign of J from EPR measurements. The exchange interactions alter the EPR spectrum through the phenomenon of exchange narrowing and collapse of the structure, which is mainly temperature-independent. The EPR spectra of a powdered sample recorded at 9.4 GHz at 300 and 120 K show little variation with T (see Figure 4). For a magnetically uncoupled Gd(III) cation ($4f^7$, $S = {}^7/_2$), a central line with $g \approx 2$ (transition $+{}^1/_2 \leftrightarrow -{}^1/_2$) plus three lateral lines at lower and higher magnetic fields (zero-field splitting, ZFS, transitions $\pm{}^7/_2 \leftrightarrow \pm{}^5/_2$, $\pm{}^5/_2 \leftrightarrow \pm{}^3/_2$, $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$) are expected. However, only the line with $g \approx 2$ is observed over a poorly resolved envelope whose features may be attributed to the incomplete collapse of the seven Gd(III) ZFS lines produced by exchange coupling of the extended 3D type between Gd(III) cations. In fact, the small difference in the distances between one Gd and its first and second Gd neighbors is against dimeric magnetic behavior. The incomplete collapse of the ZFS allows an estimation of the absolute value of the coupling J with neighboring cations within the range $0.1\ \mathrm{K} < |J|/k < 1\ \mathrm{K}$.

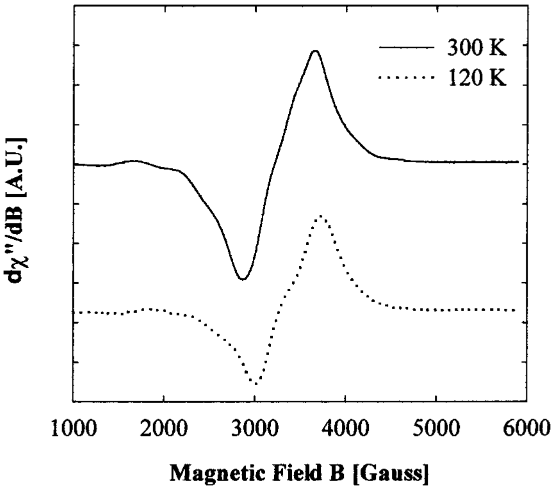

Figure 4. EPR spectra of powdered [Gd(CF_3CO_2)$_3$(phen)$_2$(H_2O)] at 300 and 120 K.

In summary we have isolated, characterized, and reported structural data for the new mononuclear gadolinium(III) mixed-ligand complex with separate O- and N-donor atoms from carboxylate and amine ligands, respectively. Magnetic susceptibility measurements showed free Gd(III) cations, and EPR measurements revealed small exchange interactions between Gd(III) cations in the 3D lattice.

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Supporting Information Available: X-ray crystallographic files in CIF format for compound [Gd(CF_3CO_2)$_3$(phen)$_2$(H_2O)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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