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Crystal and Molecular Structure and Magnetic Properties of a Trinuclear Complex Containing Exchange-Coupled $GdCu_2$ Species

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The tetradentate copper(II) Schiff base complex [*N,N'*-1,3-propylenebis(salicylaldiminato)]copper(II) (CuSALtn) reacts with gadolinium(III) and europium(III) nitrate to yield a compound of formula $(CuSALtn)_2M(H_2O)(NO_3)_3\cdot 2EtNO_2$ (M = europium(III), gadolinium(III)). The crystal structure of the gadolinium complex was determined at room temperature: the compound crystallizes in the triclinic space group $P\bar{1}$, with a = 15.694 (2) Å, b = 14.887 (1) Å, c = 10.574 (2) Å, α = 95.44 (0)°, β = 103.18 (5)°, γ = 106.95 (0)°, and Z = 2. Least-squares refinement of the structure led to a conventional R factor of 0.041. The europium(III) ion derivative was found to be isomorphous. The gadolinium(III) ion is nine-coordinated by the oxygen atoms of two CuSALtn moieties, two bidentate nitrate ions, and one water molecule. The coordination geometry can be described as a tricapped trigonal prism. The effective magnetic moment of the compound was found to increase on decreasing the temperature. The experimental points were fit to a spin-Hamiltonian model for symmetric triples of spins, to yield a weak ferromagnetic gadolinium(III)-copper(II) interaction and a weak antiferromagnetic copper(II)-copper(II) interaction. The coupling between the two copper ions was confirmed by the triplet EPR spectra of the europium(III) derivative.

Introduction

We have recently reported[2] the crystal and molecular structure of two complexes in which a gadolinium(III) ion is coordinated by two copper(II) salicylaldiminate complexes, yielding a novel trinuclear unit $GdCu_2$. Temperature-dependent magnetic susceptibility studies of these complexes showed that the effective magnetic moment increases on lowering the temperature. These results were interpreted as indicative of a moderate isotropic ferromagnetic coupling between gadolinium(III) and copper(II), with $|J|$ in the range 5–8 cm^{-1} (J is defined by the spin-Hamiltonian $H = J\mathbf{S}_1\cdot\mathbf{S}_2$). The magnetic data for these complexes were complicated by the presence of two additional copper(II) salicylaldiminate molecules in the unit cell, which, being rather well separated from the $GdCu_2$ units, were assumed to give only an additive contribution to the magnetic susceptibility of the material.

In view of the interest in the characterization of the magnetic interactions between transition-metal and lanthanide ions,[3-9] which can shed light also on the nature of the bonding in lanthanide complexes, we tried to synthesize other complexes containing $GdCu_2$ clusters, but avoiding the complication of additional copper ions present in the unit cell. We wish to report here the crystal and molecular structure of the complex obtained from the reaction of hydrated gadolinium(III) nitrate with [*N,N'*-1,3-propylenebis(salicylaldiminato)]copper(II) (CuSALtn), $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$ ($EtNO_2$ is nitroethane), which contains isolated $GdCu_2$ units, and the temperature dependence of the magnetic susceptibility in the range 4.2–300 K. The EPR spectra of the isomorphous europium(III) derivative will be reported for comparison purposes.

Experimental Section

Synthesis of the Complexes. The copper Schiff base complex, [*N,N'*-1,3-propylenebis(salicylaldiminato)]copper(II) (CuSAltn), was prepared as previously described.[10]

Table I. Crystal Data, Intensity Collection, and Structure Refinement

formula	$C_{38}H_{44}N_9O_{18}Cu_2Gd$
fw	1196.2
space group	$P\bar{1}$
a, Å	15.694 (4)
b, Å	14.887 (6)
c, Å	10.574 (4)
α, deg	95.55 (0)
β, deg	103.18 (5)
γ, deg	106.95 (0)
V, Å^3	2266.14
Z	2
d, g cm^{-3}	2.02
cryst size, mm	0.275 × 0.075 × 0.225
transm factors, max-min	0.85–0.60
scan type	ω-2θ
scan width ($\Delta\omega$), deg	1.00 + 0.3 tan θ
scan speed, deg min^{-1}	3
bkgd/scan time ratio	0.5
2θ limits, deg	2.5–30
no. of data with $F_o^2 > 3\sigma(F_o^2)$	7150
no. of variables	592
R	0.041
R_w	0.040
radiation used	Mo Kα (λ = 0.70926 Å)
temp, °C	25

Hydrated gadolinium(III) nitrate was prepared from Gd_2O_3 with nitric acid. One mmole of the gadolinium(III) salt was dissolved in ca. 20 mL of absolute ethanol. The copper complex (2.5 mmol) was dissolved in ca. 100 mL of absolute ethanol; the two solutions were warmed under stirring and then mixed. A precipitate was immediately formed and the suspension was stirred at room temperature for about 1 h. The precipitate was filtered, washed with cold ethanol-diethyl ether and dried in vacuo.

The europium(III) derivative was prepared in the same way.

These compounds analyzed satisfactorily for $M(CuSALtn)_2(NO_3)_3$ (M = Gd, Eu). Anal. Calcd for $C_{34}H_{32}N_7O_{13}Cu_2Gd$: C, 39.61; H, 3.13; N, 9.51; Cu, 12.33. Found: C, 39.81; H, 3.12; N, 9.85; Cu, 12.30. Calcd for $C_{34}H_{32}N_7O_{13}Cu_2Eu$: C, 39.80; H, 3.12; N, 9.56. Found: C, 39.40; H, 3.02, N, 9.46.

In an attempt to obtain crystals suitable for an X-ray structure determination, the compounds were dissolved in hot nitroethane and the solutions allowed to evaporate at room temperature. Green crystals were formed in 20–30 days. The compounds analyzed satisfactorily for $(CuSALtn)_2M(H_2O)(NO_3)_3\cdot 2EtNO_2$ (M = Gd, Eu). Anal. Calcd for $C_{38}H_{44}N_9O_{18}Cu_2Gd$: C, 38.06; H, 3.70; N, 10.51; Cu, 10.60. Found: C, 38.00; H, 3.69; N, 10.37; Cu, 10.65. Calcd for $C_{38}H_{44}N_9O_{18}Cu_2Eu$: C, 38.80; H, 3.57; N, 10.72. Found: C, 38.25; H, 3.53; N, 10.27.

X-ray Structure Determination of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$. A crystal of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$, shaped as

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Table II. Positional Parameters for (CuSALtn)$_2$Gd(H$_2$O)(NO$_3$)$_3$·2EtNO$_2$[a]

atom	*x*	*y*	*z*
Gd	7332	7742	6099
Cu1	7463 (1)	6580 (1)	3314 (1)
Cu2	7725 (1)	9172 (1)	3862 (1)
O1	6567 (3)	7140 (3)	3823 (4)
O2	7818 (3)	6486 (3)	5196 (4)
O3	8439 (3)	8449 (3)	4777 (4)
O4	7279 (3)	9204 (3)	5412 (4)
O5	8513 (3)	7610 (3)	8019 (4)
O6	8648 (3)	9047 (3)	7735 (5)
O7	9472 (4)	8767 (4)	9521 (5)
O8	5852 (3)	8031 (3)	6355 (4)
O9	6863 (3)	8060 (4)	8124 (4)
O10	5606 (4)	8350 (4)	8261 (5)
O11	6402 (3)	4985 (3)	2615 (4)
O12	5025 (3)	4018 (4)	2307 (4)
O13	5770 (4)	4779 (4)	4243 (4)
O14	3677 (3)	3737 (3)	3654 (4)
N1	7040 (4)	6783 (4)	1483 (5)
N2	8483 (3)	6149 (4)	3004 (5)
N3	8500 (5)	9489 (4)	2659 (5)
N4	6706 (4)	9537 (4)	2844 (5)
N5	5732 (4)	4601 (4)	3056 (5)
N6	6081 (4)	8145 (4)	7593 (6)
N7	8895 (4)	8493 (4)	8460 (6)
C1	6189 (5)	6683 (5)	974 (6)
C2	7633 (6)	6901 (6)	554 (7)
C3	8153 (5)	6189 (6)	606 (6)
C4	8885 (5)	6367 (5)	1892 (6)
C5	8788 (4)	5585 (5)	3687 (6)
C6	9304 (5)	9402 (5)	2849 (6)
C7	8194 (8)	9950 (11)	1574 (12)
C8	7280 (8)	9599 (10)	871 (8)
C9	6462 (6)	9338 (6)	1374 (7)
C10	6242 (5)	9963 (5)	3380 (8)
C11	5691 (4)	6815 (4)	3074 (5)
C12	4951 (4)	6697 (5)	3632 (6)
C13	4058 (5)	6387 (5)	2875 (7)
C14	3849 (5)	6156 (6)	1503 (7)
C15	4564 (6)	6259 (6)	932 (7)
C16	5490 (4)	6588 (5)	1688 (6)
C17	8123 (4)	5790 (4)	5621 (5)
C18	8032 (4)	5518 (5)	6832 (6)
C19	8351 (5)	4794 (5)	7275 (7)
C20	8749 (5)	4306 (5)	6535 (7)
C21	8859 (5)	4576 (5)	5359 (7)
C22	8559 (4)	5317 (4)	4891 (6)
C23	9300 (4)	8487 (4)	4766 (5)
C24	9791 (4)	8044 (5)	5628 (7)
C25	10648 (5)	8033 (5)	5600 (7)
C26	11088 (5)	8495 (5)	4736 (7)
C27	10633 (5)	8946 (5)	3872 (7)
C28	9729 (4)	8948 (4)	3857 (6)
C29	6902 (4)	9861 (4)	5766 (6)
C30	7022 (5)	10182 (5)	7078 (7)
C31	6606 (6)	10829 (6)	7456 (9)
C32	6073 (7)	11168 (6)	6542 (11)
C33	5956 (5)	10874 (6)	5231 (10)
C34	6384 (5)	10221 (5)	4807 (7)
C1*	8963 (10)	2393 (11)	−733 (14)
C2*	9379 (13)	2706 (13)	695 (17)
N1*	9206 (8)	3659 (9)	1177 (13)
O1*	9220 (7)	3648 (7)	2321 (11)
O2*	8772 (11)	4123 (11)	722 (15)
C3*	6778 (9)	2854 (9)	3527 (12)
C4*	6686 (8)	2991 (8)	2152 (11)
N2*	6739 (12)	2117 (11)	1224 (17)
O3*	6077 (19)	1813 (21)	216 (25)
O4*	7315 (17)	1847 (17)	1993 (23)
O3**	7125 (18)	2348 (17)	511 (25)
O4**	6024 (28)	1367 (30)	689 (43)
C1**	9526 (21)	3104 (21)	288 (29)
C2**	9557 (20)	4248 (18)	281 (26)

[a] Coordinates multiplied by 10^4. Standard deviations in the last significant digits are in parentheses.

Table III. Bond Distances (Å) for (CuSALtn)$_2$Gd(H$_2$O)(NO$_3$)$_3$·2EtNO$_2$[a]

Gd–Cu1	3.35 (1)	Gd–Cu2	3.37 (1)
Gd–O1	2.38 (3)	Gd–O2	2.41 (2)
Gd–O3	2.53 (5)	Gd–O4	2.38 (1)
Gd–O5	2.48 (7)	Gd–O6	2.54 (7)
Gd–O8	2.55 (1)	Gd–O9	2.47 (3)
Gd–O14	2.39 (1)	Cu1–Cu2	3.73 (3)
Cu1–O1	1.97 (2)	Cu1–O2	1.97 (3)
Cu1–N1	1.98 (3)	Cu1–N2	1.97 (1)
Cu1–O11	2.40 (2)	Cu2–O3	1.94 (3)
Cu2–O4	1.92 (3)	Cu–N3	1.95 (4)
Cu2–N4	1.96 (4)		

[a] Standard deviations in the last significant digits are in parentheses.

Table IV. Bond Angles (deg) for (CuSALtn)$_2$Gd(H$_2$O)(NO$_3$)$_3$·2EtNO$_2$[a]

O1–Gd–O3	72.1 (2)	O3–Gd–O4	63.2 (2)
O1–Gd–O4	81.6 (2)	O2–Gd–O6	112.9 (2)
O6–Gd–O8	105.9 (2)	O2–Gd–O8	139.3 (1)
O5–Gd–O9	71.2 (2)	O14–Gd–O5	88.3 (2)
O14–Gd–O9	73.4 (2)	Cu1–Gd–Cu2	67.5 (1)
O1–Gd–O2	66.9 (2)	O5–Gd–O6	50.6 (2)
O8–Gd–O9	50.6 (2)	O1–Cu1–O2	84.1 (2)
O2–Cu1–N2	91.0 (2)	N1–Cu1–N2	95.0 (2)
N1–Cu1–O1	89.6 (2)	N2–Cu1–O11	90.0 (2)
O2–Cu1–O11	95.6 (2)	O3–Cu2–O4	83.6 (2)
O3–Cu2–N3	94.1 (3)	O4–Cu2–N4	92.1 (3)
N3–Cu2–N4	95.1 (3)		

[a] Standard deviations in the last significant digits are in parentheses.

an irregular prism, of approximate dimension 0.275 × 0.075 × 0.225 mm, was used for crystal data and intensity data collection. Diffraction data were collected on a Philips PW1100 automated diffractomer equipped with a Mo X-ray tube and a graphite monochromator. Details on crystal data and intensity data collection are given in Table I. The orientation matrix and unit cell parameters were obtained from 20 machine-centered reflections with $8° \leqslant \theta \leqslant 12°$. Intensities of three check reflections measured every 120 min revealed no decay over the duration of data collection. Data were corrected for Lorentz and polarization effects, as well as for absorption.

A suitable crystal of the europium complex was analyzed with the same procedure and found to be isomorphous with the gadolinium complex.

The structure of the Gd derivative was solved in the $P\bar{1}$ space group by locating the Gd and Cu atoms using direct methods. All the remaining non-hydrogen atoms were located by Fourier and difference Fourier maps and least-squares refinement.

Programs used in the crystallographic calculations are given in ref 11. Atomic scattering factors were taken from a standard source.[12]

Extra peaks of about 1.5 e Å^{-3} appearing in the difference Fourier maps when *R* was about 8% have been assigned to two nitroethane molecules according to the elemental analysis. Extra peaks of lower intensities still remained around the nitroethane molecules, indicating that some disorder exists. Since the *R* values were most insensitive to the position of the solvent molecules it was not possible to solve the disorder. The highest extra peaks were found near the carbon and oxygen atoms of the nitroethane molecules and have been included in the refinement with 0.5 site occupation factors. Hydrogen atoms were located in calculated positions (C–H = 1.08 Å) and introduced in structure factor calculations with an isotropic thermal parameter 20% larger than that of the corresponding carbon atom.

The refinement converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.041$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.040$ with $w = 0.94/\sigma^2(F_o)$. Some residual peaks in the last difference Fourier map were 0.9–0.8 e A^{-3} and were located around the solvent molecules. All the other peaks were less than 0.6 e A^{-3}. Final atomic positional parameters for non-hydrogen atoms are collected in Table II. Atomic positional parameters for hydrogen atoms and thermal parameters for non-hydrogen atoms are available as supplementary material (Tables SI and SII). A listing of observed and calculated structure factors is also available.

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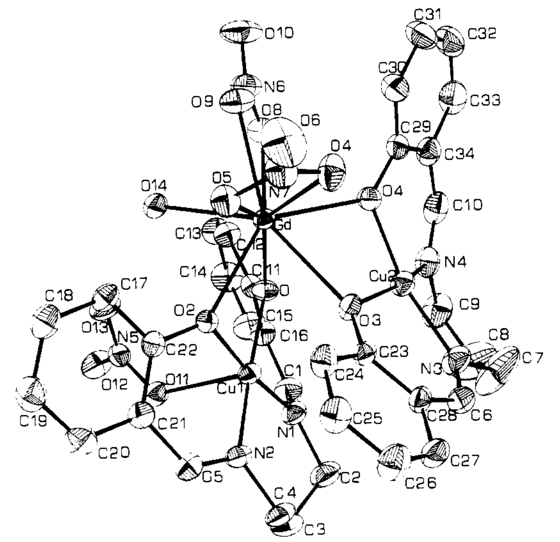

Figure 1. ORTEP view of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$.

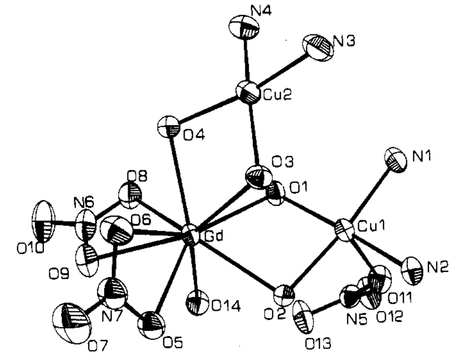

Figure 2. Schematic view of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$. Only the metals and the coordinated atoms are shown.

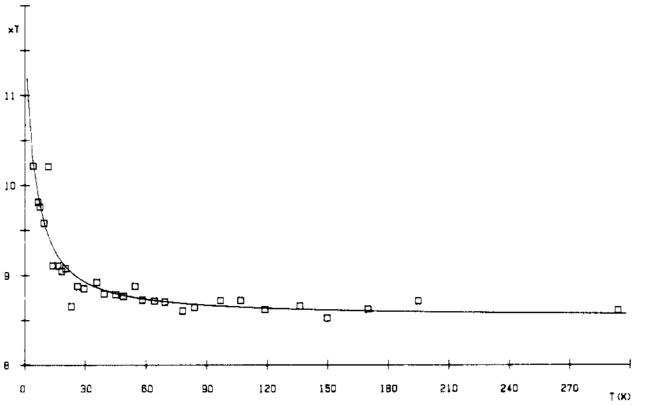

Figure 3. Temperature dependence of the χT product for $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$ in the range 4.2–300 K. Experimental points are shown as squares. The curve was calculated as dicussed in the text.

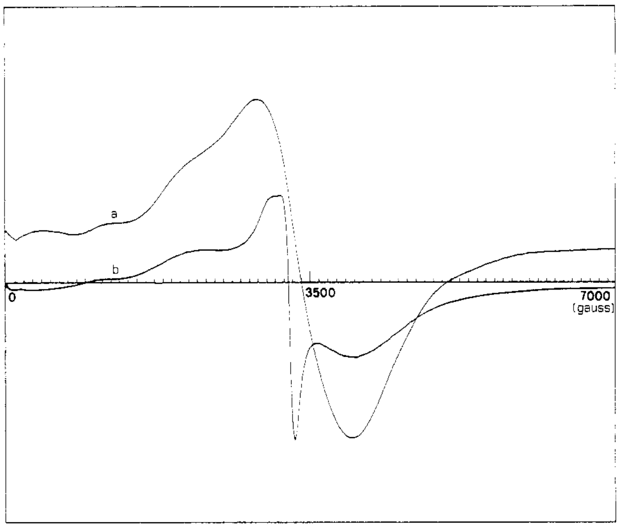

Figure 4. Polycrystalline powder EPR spectra of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$ at room temperature (a) and 4.2 K (b).

Magnetic and EPR Measurements. The EPR spectra were recorded with a Bruker ER200 spectrometer. The magnetic susceptibilities were measured in the range 4.2–300 K with a Faraday balance equipped with a Cahn R100 microbalance, a Bruker electromagnet operanting at 2 T, and an Oxford Instruments continuous-flow CF200 cryostat. The internal helium pressure was adjusted at 10^{-1} mmHg. The system was calibrated with $Ni(en)_3(S_2O_3)$.

Results and Discussion

Structural Description of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$. The crystal structure of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$ consists of trinuclear species $(CuSALtn)_2Gd(H_2O)(NO_3)_3$ and of two nitroethane molecules. In the trinuclear species the gadolinium(III) ion is nine-coordinated by four oxygen atoms of two bidentate nitrate ions, four oxygen atoms of two CuSALtn molecules and a water molecule. The third nitrate ion is coordinated to one of the two copper atoms of CuSALtn. The bond distances of the gadolinium(III) ion to the nine-coordinated oxygen atoms are in the range 2.38–2.55 Å. Selected bond distances and angles are collected in Tables III and IV.

The coordination polyhedron around the gadolinium(III) ion is best described as a tricapped trigonal prism, corresponding to one of the two limit geometries for nine-coordination.[13] An ORTEP view of the trinuclear $GdCu_2$ moiety is shown in Figure 1. A simplified view of the molecule showing only the metals and the coordinated atoms is given in Figure 2. One of the two trigonal faces of the prism is defined by the oxygen atoms of one CuSALtn moiety (O3 and O4) and by one oxygen atom of the second CuSALtn (O1), while the other face is defined by the water molecule (O14) and two oxygen atoms of two different nitrate ions (O5 and O9). The atoms capping the side faces of the prism are the second oxygen atom of a CuSALtn molecule (O2) and the oxygen atoms of two nitrate ions (O6 and O8). The planes of the two triangular faces are roughly parallel to each other, making an angle of 11.4°, while the plane of the three capping atoms is almost parallel, 1.4°, with the O5–O9–O14 plane and make an angle of 10.3° with the O1–O3–O4 plane.

The two (CuSALtn) moieties are much different from each other. In fact the coordination around Cu1 is tetragonal pyramidal, with an axial nitrate at 2.40 (1) Å, while the coordination around Cu2 is square planar, with a marked tetrahedral distorsion. The N4–Cu2–O3 and N3–Cu2–O4 angles, which should be close to 180° for square-planar coordination, are 162.8 (2) and 161.4 (2)°, respectively. The bidentate nitrate ions are bound to the gadolinium(III) ion in a slightly asymmetric fashion. The two oxygen–gadolinium distances differ in fact by as much as 0.06–0.08 Å.

Magnetic Data. The temperature dependence of the magnetic susceptibility of $(CuSALtn)_2Gd(H_2O)(NO_3)_3\cdot 2EtNO_2$ in the range 4.2–300 K is shown in Figure 3 in the χT vs. T form. The room-temperature magnetic susceptibility agrees well with the sum of those of one gadolinium(III) and two copper(II) ions, but a marked increase in χT is observed below 30 K. If the three spins $S_{Gd} = {}^7/_2$ and $S_{Cu1} = S_{Cu2} = {}^1/_2$ are allowed to interact, the resulting total spin states are one $S = {}^9/_2$, one $S = {}^5/_2$, and two $S = {}^7/_2$. The observed effective magnetic moment at 4.2 K is 9.04 μ_B, which indicates that at low temperature the population of the $S = {}^9/_2$ state increases. The experimental points were fit first to a Curie–Weiss law, which yielded $\Theta = 0.54$ (3) K in agreement with a slight ferromagnetic interaction. In order to relate the

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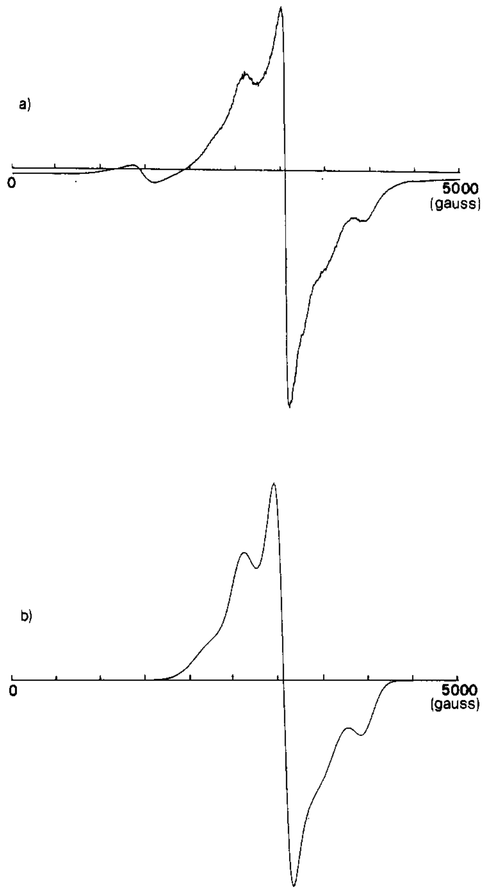

Figure 5. Polycrystalline powder EPR spectra of $(CuSALtn)_2Eu(H_2O)(NO_3)_3{\cdot}2EtNO_2$ at 4.2 K observed (a) and calculated (b) with the fit parameters.

observed deviation from the Curie law to the Gd–Cu and Cu–Cu interactions, χT was fit by using the spin-Hamiltonian

$$H = J(\mathbf{S}_{Gd}{\cdot}\mathbf{S}_{Cu1} + \mathbf{S}_{Gd}{\cdot}\mathbf{S}_{Cu2}) + J'\mathbf{S}_{Cu1}{\cdot}\mathbf{S}_{Cu2}$$

The two copper ions were considered to be identical for the sake of simplicity. The calculated curve is shown in Figure 3 and the best-fit parameters are $g = 1.988$ (1), $J = -1.22$ (1) cm^{-1}, and $J' = 3.6$ (3) cm^{-1}. The sign of J corresponds to a ferromagnetic Gd–Cu interaction and that of J' to an antiferromagnetic Cu–Cu interaction.

EPR Data. The polycrystalline powder EPR spectra of $(CuSALtn)_2Gd(H_2O)(NO_3)_3{\cdot}2EtNO_2$ at room and liquid-helium temperatures are shown in Figure 4. They are rather uninformative, in the sense that they show several features, dominated by one at $g = 2$, difficult to interpret. The substantial similarity of the high- and low-temperature spectra shows that no dramatic change in the population of the levels occurs. Also it can be noted that no feature can be obviously assigned to a free copper ion, thus confirming the presence of a coupling between the metal ions.

More informative are the spectra of the analogous europium(III) derivative, whose polycrystalline powder EPR spectra at 4.2 K are shown in Figure 5. These spectra are typical of a triplet,[14] showing the characteristic feature at half-field due to the $\Delta M = \mp 2$ transition. The overall appearance of the spectrum in the $\Delta M = \mp 1$ region is similar to that of copper(II) dinuclear complexes, recently reported,[15,16] which were characterized by single-crystal spectra and were found to have $E/D \simeq 1/3$. Using the same approach, it is possible to assign the $EuCu_2$ spectra in the following way: the intense peaks at 0.26 and 0.39 T to the two components parallel to y, the feature at 0.31 T to x, and the z components at 0.34 T and below 0.26 T. A reasonable fit to this assignment can be reached with $g_x = 2.19$ (1), $g_y = 2.06$ (1), $g_z = 2.34$ (1), $D = 0.066$ cm^{-1}, and $E = 0.0215$ cm^{-1}. The spectrum calculated with these parameters is compared with the experimental one in Figure 5.

Since europium(III) has a ground $^7F_0$ state, it is certainly diamagnetic at low temperature; therefore, the observed spectrum must be attributed to the two coupled copper ions. The extent and the sign of the coupling cannot be determined from the EPR spectrum, but it shows that the triplet state is populated at 4.2 K.

The calculated principal g values are fairly anisotropic, presumably due to the fact that the two copper coordination polyhedra are not equivalent, one being tetrahedral and the other square pyramidal. Further in the simulation of the powder spectra it was assumed that the **g** and **D** tensors are parallel to each other, but this assumption is presumably not correct. Single-crystal studies are in progress in order to make a detailed analysis of the spin-Hamiltonian tensors in this compound.

If we make the assumption that the observed zero field splitting of the triplet is due to the magnetic dipolar interaction between the two unpaired electrons of the two copper ions,[17] it is possible to calculate D and E from the crystal structure data of the gadolinium analogue and the g values obtained from the analysis of the spectra. The calculated D value is not far from the observed one, but the E/D ratio is much closer to the axial than to the rhombic limit. It seems possible then that the discrepancy is due to a nonneglectable exchange contribution to the zero field splitting.[17]

Conclusions. The magnetic data of $(CuSALtn)_2Gd(H_2O)(NO_3)_3{\cdot}2EtNO_2$ show that a coupling between gadolinium(III) and copper(II) does exist and that it is isotropic and ferromagnetic in nature, thus confirming the analogous data previously obtained for two other $GdCu_2$ triples. The actual value of J calculated in this case is smaller than in the two previous ones, but given the intrinsic low accuracy in the determination of the negative (ferromagnetic) coupling constants,[18,19] we feel it more appropriate not to discuss in detail the differences. It is worth noting however that both for seven- and for nine-coordinated central gadolinium(III) ions the coupling to copper(II) is ferromagnetic, suggesting that the coordination geometry does not strongly determine the exchange-coupling mechanism. Probably this is dominated by the interaction of the magnetic orbitals on copper with those f orbitals on gadolinium that are not involved in the bonding to the bridging oxygen atoms. In all the three $GdCu_2$ species we studied, the fit of the experimental susceptibility required an antiferromagnetic coupling between the two terminal copper ions. The EPR spectra of the europium(III) derivative showed that indeed a triplet state is populated at 4.2 K. The fact that the observed zero field splitting parameters of this triplet deviate from the values expected on the basis of a purely magnetic dipolar coupling suggests that the two copper ions are actually exchange-coupled, confirming the magnetic data for the gadolinium derivative. The fact that the two copper ions are coupled confirms also that the f orbitals of gadolinium are involved in a superexchange interaction with the d orbitals.

Registry No. $(CuSALtn)_2Gd(H_2O)(NO_3)_3{\cdot}2EtNO_2$, 99808-49-8; $(CuSALtn)_2Eu(H_2O)(NO_3)_3$, 99808-50-1; CuSALtn, 21051-65-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and calculated and observed structure factor amplitudes for $(CuSALtn)_2Gd(H_2O)(NO_3){\cdot}2EtNO_2$ (46 pages). Ordering information is given on any current masthead page.

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