

Crystal Structure and Magnetic Properties of a Novel Cu^{II}Nd^{III} Heterodinuclear Schiff Base Complex

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Z. Naturforsch. **59b**, 530 – 534 (2004); received November 18, 2003

The crystal structure of $L'Cu(Me_2CO)Nd(NO_3)_3$ ($L' = N,N'$ -bis(2-hydroxy-3-methoxybenzylidene)-ethylenediamine) was determined and the magnetic properties of the complex were investigated. $(C_{18}H_{18}N_2O_4)Cu(C_3H_6O)Nd(NO_3)_3$, monoclinic, space group $P2_1/c$, with $a = 9.8792(9)$, $b = 18.904(4)$, $c = 15.667(2)$ Å, $\beta = 95.360(10)^\circ$, $V = 2913.1(8)$ Å³, $Z = 4$. The central region of the complex is occupied by Cu^{II} and Nd^{III} ions which are bridged by two phenolato oxygen atoms of the ligand. The copper ion adopts a square-based 4+1 coordination made, the basal N_2O_2 donors being afforded by the ligand while the axial position is occupied by the oxygen atom of the acetone molecule. The Nd^{III} ion is deca-coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of L and six oxygen atoms from the three bidentate nitrate ions. The Cu \cdots Nd separation is 3.466(2) Å. The χT versus T plots, χ being the molar magnetic susceptibility per Cu^{II}Nd^{III} unit and T the temperature, has been measured in the 4.5 – 299.6 K temperature range. The magnetic properties of the investigated compound are dominated by the crystal field effect on the Nd^{III} site, masking the magnetic interaction between the paramagnetic centers.

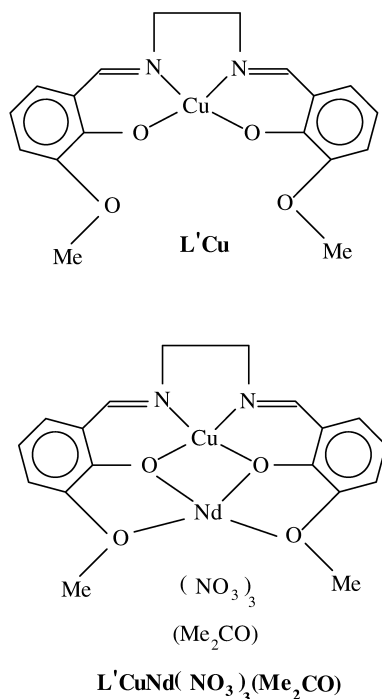
Key words: Heterodinuclear Complex, Copper, Neodymium, Crystal Structure, Magnetic Properties

Introduction

In the past two decades or so, a large number of heteropolymetallic compounds have been described. The studies of these compounds have often been performed either in relation to the modeling of some metalloenzymes containing several kinds of metal ions or with the perspective to design novel molecular materials, in particular molecule-based magnets, with a particular emphasis on the magnetic properties [1]. The main idea emerging from those studies is that the interaction between two nonequivalent magnetic centers may lead to situations which cannot be encountered with species containing a unique kind of spin carrier. In fact, the recent investigations of the magnetic properties of heteropolymetallic compounds have made important contributions to the development of molecular ferromagnetism. Magnetic studies on the d -transition metal polynuclear complexes have shown tremendous progress during the latest decade regarding experimental and theoretical fields. Procedures have become fairly well established for predicting the mag-

netic properties of a polynuclear d -transition metal complex [2,3]. On the other hand, magnetic investigations concerning mixed-metal complexes comprising d - and f -transition metal ions have been overlooked until recently due to the very weak interaction and the large anisotropic effect of lanthanoid ions. The rather large and anisotropic magnetic moments of most of the lanthanide(III) ions Ln^{III} , make these ions appealing building blocks in the molecular approach of magnetic materials. Numerous compounds containing a Ln^{III} ion and paramagnetic species such as a transition metal ion [3–9] or an organic radical [9, 12] have been described.

Very recently, we studied the crystal structure and magnetic properties of a heterodinuclear Cu^{II}Ce^{III} complex, $LCu(Me_2CO)Ce(NO_3)_3$ ($L = N,N'$ -propylene-bis(3-methoxysalicylideneimine)) [13]. In this study, we have synthesized a new heterodinuclear Cu^{II}Nd^{III} compound, $L'Cu(Me_2CO)Nd(NO_3)_3$ ($L' = N,N'$ -bis(2-hydroxy-3-methoxybenzylidene)-ethylenediamine) and determined its crystal structure by X-ray diffraction. We have also measured magnetic



susceptibilities in the temperature range 4.5–299.6 K using a SQUID magnetometer in an attempt to gain more information on the magnetic properties of Ln^{III} polynuclear complexes.

Experimental Section

Preparation

The hetero-dinuclear Cu^{II}Nd^{III} complex, L'Cu(Me₂CO)Nd(NO₃)₃ (L' = N,N'-bis(2-hydroxy-3-methoxybenzylidene)ethylenediamine) was prepared in two steps. In the first step, the Schiff base ligand was synthesized by reaction of ethylenediamine and 2-hydroxy-3-methoxybenzaldehyde in a 1:2 molar ratio at room temperature. The Schiff base was obtained in the form of yellow crystals. After that, the Schiff base ligand (1 mmol) in hot methanol (50 ml) and a solution of Cu(CH₃COO)₂·H₂O (1 mmol) in hot methanol (40 ml) was added. Green prismatic crystals of (L'Cu) were filtered off and dried in an oven at 343 K.

In the second step, for the preparation of the Cu^{II}Nd^{III} complex, an acetone solution (10 ml) of Nd(NO₃)₃·H₂O (1 mmol) was added to a suspension of the copper(II) complex, L'Cu (1 mmol), in acetone (40 ml). Soon, the suspension became clear and red crystals began to precipitate, which were collected by suction filtration and washed with cold acetone and finally dried in air. C₂₁H₂₄N₅O₁₄CuNd (778.23): calcd. C 32.4, H 3.1, N 9.0, Cu 8.2, Nd 18.5; found C 33.9, H 3.2, N 8.9, Cu 8.4, Nd 18.9.

Table 1. Crystallographic data.

Sum formula	C ₂₁ H ₂₄ CuNdN ₅ O ₁₄
f _w (g·mol ⁻¹)	778.23
Space group	P2 ₁ /c
a = 9.8792(9) Å	
b = 18.904(4) Å	β = 95.360(10)°
c = 15.667(2) Å	
Vol [Å ³]	2913.1(8)
Z	4
D _{calc} (g·cm ⁻³)	1.774
μ [cm ⁻¹]	2.480
F(000)	1544
Index ranges	−12 ≤ h ≤ 12, 0 ≤ k ≤ 23, 0 ≤ l ≤ 19
Reflections collected	5703
Independent reflections	5699 [R(int) = 0.029]
Data / restraints / parameters	5703 / 0 / 379
Goodness-of-fit on F ²	1.331
Final R indices [I > 2σ(I)]	R = 0.0286, wR = 0.0781
Largest diff. peak and hole	0.581 and −1.165 e. Å ⁻³

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [14] using a single crystal with dimension 0.05 × 0.10 × 0.20 mm³ with a graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections (2.06° ≤ θ ≤ 10.93°) carefully centered on the diffractometer. The standard reflections were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [14]. The structure was solved by SHELXS-97 [15] and refined with SHELXL-97 [16]. All nonhydrogen atoms were treated anisotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Selected bond lengths and angles are summarized in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 224212 [17].

Susceptibility measurements

Magnetic susceptibility data were collected on a powdered sample of the compound with use of a SQUID-based sample magnetometer on a QUANTUM Design Model PPMS instrument in the temperature range 4.5–299.6 K. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [18]. The applied field was 10 KOe.

Table 2. Selected bond lengths [Å] and angles [°].

Cu1–N1	1.937(4)	Nd1–O1	2.638(3)
Cu1–N2	1.912(3)	Nd1–O2	2.419(2)
Cu1–O2	1.895(3)	Nd1–O3	2.412(2)
Cu1–O3	1.904(2)	Nd1–O4	2.644(2)
Cu1–O3	1.904(2)	Nd1–O5	2.502(3)
Cu1–O14	2.600(3)	Nd1–O6	2.485(3)
Nd1–O7	2.568(3)	Nd1–O8	2.574(3)
Nd1–O9	2.490(3)	Nd1–O10	2.546(3)
Cu1–O2–Nd1	106.27(9)	O3–Nd1–O2	62.84(8)
Cu1–O3–Nd1	106.24(10)	O3–Nd1–O6	74.44(12)
O2–Cu1–O3	83.03(9)	O3–Nd1–O6	74.44(12)
O2–Cu1–N2	172.26(14)	O2–Nd1–O6	99.72(12)
O3–Cu1–N2	96.85(13)	O3–Nd1–O9	116.85(9)
O2–Cu1–N1	95.67(13)	O2–Nd1–O9	118.36(9)
O3–Cu1–N1	173.12(16)	O6–Nd1–O9	141.52(12)
N2–Cu1–N1	83.53(16)	O3–Nd1–O5	101.21(11)
O2–Cu1–O14	96.89(11)	O2–Nd1–O5	76.06(11)
O3–Cu1–O14	96.01(11)	O6–Nd1–O5	49.49(12)
N2–Cu1–O14	90.82(14)	O9–Nd1–O5	141.87(10)
N1–Cu1–O14	90.85(16)	O3–Nd1–O7	123.02(8)
O2–Nd1–O7	166.51(11)	O6–Nd1–O7	72.26(14)
O9–Nd1–O7	71.29(11)	O5–Nd1–O7	90.59(13)
O3–Nd1–O4	60.80(7)	O2–Nd1–O4	122.28(8)
O6–Nd1–O4	76.62(11)	O9–Nd1–O4	78.38(9)
O5–Nd1–O4	126.04(10)	O7–Nd1–O4	67.30(8)

Results and Discussion

The ORTEP view [19] of the molecular structure is shown in Fig. 1. The unit cell contains four formula units. The central region is occupied by Cu^{II} and Nd^{III} ions which are bridged by two phenolato oxygen atoms of the ligand. The intramolecular Cu...Nd distance is 3.466(2) Å.

The Cu^{II} ion adopts a square-based 4+1 coordination mode, the basal N₂O₂ donors being afforded by the ligand while the axial position is occupied by the oxygen atom of the acetone molecule. The Cu^{II} centre is –0.097(2) Å above the mean N₂O₂ coordination plane. The average Cu–O and Cu–N distances in the ligand are 1.890(3) and 1.925(4) Å, respectively, and are within the usual range observed for copper coordinated to Schiff bases [7, 8, 20]. The axial bond distance between Cu1 and the O atom of the acetone molecule is 2.600(3) Å, longer than the other Cu–O bond distances. This significant difference is also observed in other complexes with Cu^{II} extra-coordinated by solvent molecules [14, 21, 22].

The Nd^{III} ion is deca-coordinated. In addition to the two phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of L' and six oxygen atoms of the three bidentate nitrate ions. The average distance between the Nd^{III} ion and

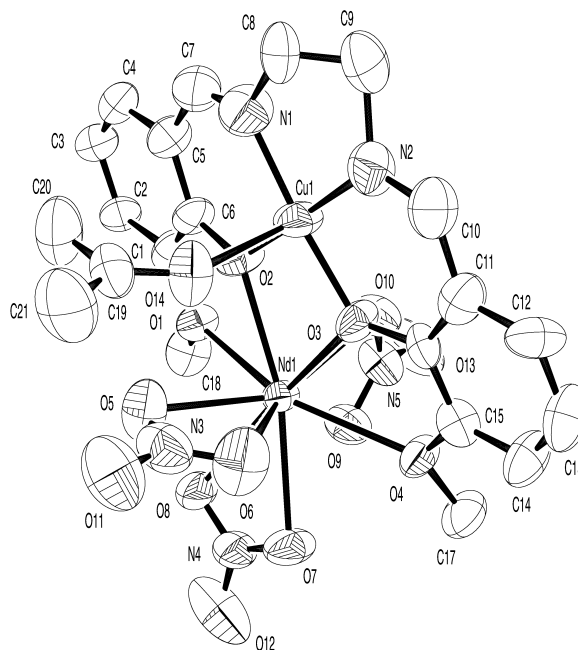


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms have been omitted for clarity.

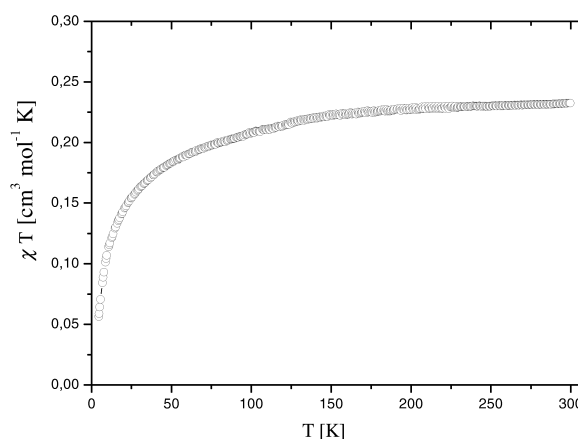


Fig. 2. Plot of χT versus temperature.

the O atoms of the nitrate ions is 2.528(3) Å. The range of the Nd–O bond lengths is rather large (from 2.412(3) to 2.638(3) Å) with significant differences between the phenolic, methoxy, and nitrate oxygen atom. The shortest Nd–O bond (2.412(3) Å) is related to the phenolic oxygen atoms while the largest bond (2.644(2) Å) involves the methoxy oxygen atom. The Nd1–O2–Cu1 and Nd1–O3–Cu1 bridging angles are 106.3(1) and 106.2(1)°, respectively. The maximum

deviation from the bridging plane defined by atoms Cu1, O2, O3 and Nd1 is $-0.101(1)$ Å for the Cu1 atom. The dihedral angle between the NdO(2)Cu and NdO(3)Cu planes is $15.7(2)^\circ$. The torsion angles N1–Cu1–O2–Nd1 and N2–Cu1–O3–Nd1 are $-176.3(1)$ and $177.3(1)^\circ$. The unique half of the Schiff base ligands of the complex is reasonably planar. The maximum deviation from the plane defined by atoms C1, O1, C2–C8, N1 and O2 is $0.101(2)$ Å for the O2 atom, and for atoms O4, O3, C9–C17 and N2 it is $0.421(4)$ Å for the C17 atom. However, the whole ligand L' is not exactly planar since the two halves are twisted with respect to one another. The least-squares planes through each half of the L' ligand are inclined at an angle of $4.0(1)^\circ$ in the complex.

The separations between metal ions belonging to neighbouring molecules are large (Nd...Cu = 13.61 Å, Nd...Nd = 10.99 Å, and Cu...Cu = 10.64 Å) and preclude any significant intermolecular magnetic interaction.

The magnetic susceptibilities and the χT products are shown as a function of temperature in Fig. 2. The major difficulties in analyzing the magnetic properties of the Cu^{II}–Nd^{III} couple arise from the fact that the ground state of the Nd^{III} ion has a first-order angular momentum which prevents the use of a spin-only Hamiltonian for isotropic exchange [23, 24]. The joint effects of the crystal field and orbital contribution can result in an anisotropy of the magnetic susceptibility and exchange interaction. Informative magnetic susceptibility measurements have been performed for

the investigated compound. As a general trend, for the complexes of the paramagnetic Ln^{III} ions of the first half of the series the χT versus T curves are characterized by a continuous decrease as the temperature is lowered (Fig. 2.). Kahn *et al.* [17] concluded that for the $4f^1 - 4f^6$ configuration of Ln^{III}, angular and spin momenta are antiparallel in $^{2S+1}L_J$ free-ion ground state ($\mathbf{J} = \mathbf{L} - \mathbf{S}$). A parallel alignment of the Cu^{II} and Ln^{III} spin momenta would lead to an antiparallel alignment of the angular momenta, that is to an overall antiferromagnetic interaction. Conversely, for the $4f^8 - 4f^{13}$ configurations ($\mathbf{J} = \mathbf{L} + \mathbf{S}$), a parallel alignment of the Cu^{II} and Ln^{III} spin momenta would result in an overall ferromagnetic interaction. Recently, an experimental approach has been developed to determine the nature of the magnetic interaction in Ln^{III}–Cu^{II} [4, 18]. It consists of comparing the magnetic properties of two series of isostructural compounds, one composed of Ln^{III}–M pairs and the other of Ln^{III}–M' pairs, M being a paramagnetic and M' a diamagnetic $3d$ ion. This method was applied to infinite [18] and finite compounds [3]. Concerning the finite compounds, ferromagnetic interactions were observed for Ln = Gd, Tb, Dy, Ho and Er, and antiferromagnetic interactions for Ln = Ce, Nd, Sm, Tm and Yb.

Acknowledgement

This work was supported by the Scientific Research Project Fund of University of Ankara under grant number 2002-07-45-004.

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