

Structural and EPR Studies on Single-Crystal and Polycrystalline Samples of Copper(II) and Cobalt(II) Complexes with N₂S₂-Based Macrocyclic LigandsAbel Tamayo,^{†‡} Jaume Casabó,[†] Lluís Escriche,^{*,†} Pablo González,[‡] Carlos Lodeiro,^{*,‡} Alberto C. Rizzi,[§] Carlos D. Brondino,^{*,§} M. C. G. Passeggi,^{||} Raikko Kivekäs,[⊥] and Reijo Sillanpää[#]

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The properties of Cu(II) and Co(II) complexes with oxygen- or nitrogen-containing macrocycles have been extensively studied; however, less attention has been paid to the study of complexes containing sulfur atoms in the first coordination sphere. Herein we present the interaction between these two metal ions and two macrocyclic ligands with N₂S₂ donor sets. Cu(II) and Co(II) complexes with the pyridine-containing 14-membered macrocycles 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L**) and 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L1**) have been synthesized. The X-ray structural analysis of { [Co(ClO₄)(H₂O)(**L**)] [Co(H₂O)₂(**L**)] } (ClO₄)₃ shows two different metal sites in octahedral coordination. The EPR spectra of powdered samples of this compound are typical of distorted six-coordinated Co(II) ions in a high-spin (*S* = 3/2) configuration, with the ground state being *S* = 1/2 (*g*₁ = 5.20, *g*₂ = 3.20, *g*₃ = 1.95). The EPR spectrum of [Cu(ClO₄)(**L**)](ClO₄) was simulated assuming an axial *g* tensor (*g*₁ = *g*₂ = 2.043, *g*₃ = 2.145), while that of [Cu(ClO₄)(**L1**)](ClO₄) slightly differs from an axial symmetry (*g*₁ = 2.025, *g*₂ = 2.060, *g*₃ = 2.155). These results are compatible with a Cu(II) ion in square-pyramidal coordination with N₂S₂ as basal ligands. Single-crystal EPR experiment performed on [Cu(ClO₄)(**L1**)](ClO₄) allowed determining the eigenvalues of the molecular *g* tensor associated with the copper site, as well as the two possible orientations for the tensor. On the basis of symmetry arguments, an assignment in which the eigenvectors are nearly along the Cu(II)–ligand bonds is chosen.

Introduction

The study of the structural, spectroscopic, and electronic properties of metal centers present in biological systems is crucial to understand their role in nature. These centers are often modeled by using small molecules containing donor atoms that reproduce the coordination around the metal ion.¹

The use of simple metal-containing systems with low molecular weight ligands is useful to understand the correlation between magnetic, electronic, and structural properties in more complex systems.² For this reason, the synthesis of complexes oriented to mimic metal sites of different types of metalloproteins constitutes an important branch in both inorganic and organic chemistry. Copper and cobalt are present in a diverse group of metalloenzymes, in which the metal ions are coordinated to N, O, and S atoms.³ In type I Cu centers (e.g., amicyanin, plastocyanin, and pseudoazurin), the Cu(II) ion is coordinated in a trigonal-planar fashion by 2 histidines and 1 cysteine (N2S coordination) with one or

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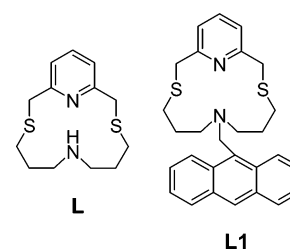
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two weakly interacting axial ligands (S or O), whereas type II copper centers (e.g., dioxygenase, monooxygenases, nitrite reductase) exhibit a square-planar (square pyramidal is also found in literature) coordination by N or N/O ligands.⁴ S ligands were only detected in the diethylthiocarbamate inhibited form of the enzyme quercetin 2,3-monooxygenase.⁵ Copper can be also found forming part of multinuclear units in several enzymes. Several metalloproteins containing cobalt coordinated to histidine, aspartic, and glutamic acids, such as methionine aminopeptidase, prolidase, glucose isomerase, methylmalonyl-CoA carboxytransferase, lysine 2,3-aminomutase, and aldehyde decarboxylase, were also characterized.⁶ Cobalt has been also used to substitute for other metal ions present in metalloproteins because of its high sensitivity to the coordination site geometry, which allows one to gather information about changes of metal sites in proteins during protein function.⁷

The biomimicking of the metal sites in metalloproteins can be accomplished designing special coordination complexes containing different ligands. Although one must be careful to prevent overinterpretations of the information derived from these simplified models, the use of simple systems has provided valuable information about the physicochemical properties of different Cu(II)- or Co(II)-containing metalloenzymes.^{2,8} The structural and spectroscopic properties of Cu(II) and Co(II) complexes with oxygen- or nitrogen-containing macrocyclic ligands have been extensively studied. However, less attention has been paid to the study of Cu(II) and Co(II) complexes containing sulfur atoms in the first coordination sphere. According to the theory of hard and soft acids and bases, S-containing ligands are softer than those with only oxygen or nitrogen as donor atoms. This fact defines the electronic structure of the complexes, because the lower the hardness of the ligand, the greater the covalent character of its bonds with the cation.⁹ Since both Cu(II) and Co(II) ions are paramagnetic, EPR has been a powerful tool in the magnetic and electronic characterization of complexes containing these metal ions. The higher covalent character of the Cu–S bond lowers the orbital reduction factor,¹⁰ determining that the Cu(II) complexes containing S in equatorial positions show generally *g* values

Scheme 1



lower than those with nitrogen or oxygen ligands. EPR studies have been only limited to reports on powder and solution samples, but, to the best of our knowledge, there is no report on the orientation of the *g* tensor with respect to the molecular frame in compounds with Cu–S bonds, information that can be only obtained through single-crystal EPR experiments. Less information exists about the magnetic and electronic properties of Co(II) compounds. Co(II) ions show a ground state with both spin and orbital degeneracy and a fast relaxing behavior, which introduces additional complications in the measurement and analysis of the EPR data. Co(II) ions can be present in two different spin configurations (high, $S = 3/2$, or low, $S = 1/2$).¹¹ The adopted spin configuration of Co(II) compounds depends on the magnitudes of the energy gap between the metal orbitals relative to the mean spin pairing energy. High-spin Co(II) ions are commonly found in octahedral or tetrahedral compounds. In contrast, Co(II) ions in tetragonal complexes show low-spin behavior, with EPR spectra rather different from that of high-spin complexes.¹¹

This paper describes the synthesis, structural, and EPR studies of Cu(II) and Co(II) complexes with the sulfur-containing ligands 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L**) and 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L1**) (see Scheme 1). X-ray data are presented for $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$. Ligands **L** and **L1** have a pyridyl–thioether macrocycle as a receptor unit. In addition, **L1** has an anthracene moiety linked through a methylene group to the macrocyclic unit. The presence/absence of an anthracenylmethyl group bonded to the aliphatic amine changes both the hydrophobicity and the coordination properties of the ligands, since such amine group is secondary for **L** and tertiary for **L1**. The *g*-tensor orientation of the Cu(II) ion in $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ is studied by single-crystal EPR spectroscopy and analyzed in relation with the structural data.

Experimental Section

General Remarks. All syntheses were carried out using standard Schlenk techniques. Organic reagents and transition metal salts were purchased from Aldrich and used as received. Elemental analyses were performed on a Carlo Erba EA-1108 instrument by the Chemical Analysis Service of the Universitat Autònoma de Barcelona. Mass spectra were recorded using a HP298S GC/MS system. Conductivity measurements were carried out using a

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Table 1. Crystallographic and Refinement Data for {[Co(ClO₄)(H₂O)(L)][Co(H₂O)₂(L)]}(ClO₄)₃

empirical formula	C ₂₆ H ₄₆ Co ₂ Cl ₄ N ₄ S ₄ O ₁₉
fw	1106.57
temp (K)	173(2)
wavelength (Å)	0.710 73
cryst size (mm)	0.30 × 0.28 × 0.04
color/habit	violet/plate
cryst syst	orthorhombic
space group	<i>P</i> 2 ₁ <i>ab</i>
<i>a</i> (Å)	14.0651(2)
<i>b</i> (Å)	16.4986(2)
<i>c</i> (Å)	18.1599(3)
<i>V</i> (Å ³)	4214.09(11)
<i>Z</i>	4
<i>D</i> _c (Mg m ⁻³)	1.744
<i>μ</i> (mm ⁻¹)	1.318
<i>F</i> (000)	2272
<i>θ</i> range for data collcn (deg)	2.21–24.71
index ranges	–16 ≤ <i>h</i> ≤ 16 –19 ≤ <i>k</i> ≤ 19 –21 ≤ <i>l</i> ≤ 21
reflens colld	20 947
indpdnt reflens	6739 (<i>R</i> _{int} = 0.0645)
data/restraints/params	6739/3/552
goodness of fit on <i>F</i> ²	1.055
final <i>R</i> indices	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.0874
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0656, <i>wR</i> ₂ = 0.0951
largest diff peak and hole (e Å ⁻³)	0.611 and –0.447

Cyberscan 500 conductimeter. IR spectra were recorded using a Perkin-Elmer FT-1710 instrument. Absorption spectra were recorded on a Shimadzu spectrophotometer UV-2510-PC. Macrocycle **L** was prepared as reported in the literature.¹² Macrocycle **L1** and complex [Cu(ClO₄)(**L1**)](ClO₄) were synthesized as previously reported.¹³

EPR Measurements. X-band CW EPR spectra of polycrystalline and single-crystal samples were taken with a Bruker ER200 spectrometer using a rectangular cavity with 100 kHz field modulation and equipped with an Oxford continuous-flow cryostat. The EPR parameters of powder samples were obtained from spectral simulations using the program Simfonia (v. 1.25, Bruker Instruments Inc.). Powder samples for EPR were obtained by grinding single crystals. The samples for the single-crystal EPR experiments were oriented by gluing one external crystal face to a cleaved KCl cubic holder, which defines a set of orthogonal laboratory axes. The habit of the crystals was determined by measuring the angles between crystal faces using a goniometric microscope. The sample holder was introduced into a 4 mm OD quartz tube and positioned in the center of the microwave cavity (see refs 14 and 15 for details). The tube was attached to a goniometer, and the sample was rotated in steps of 10° with the magnetic field in three crystal planes.

X-ray Crystal Structure Determinations. A single crystal of {[Co(ClO₄)(H₂O)(L)][Co(H₂O)₂(L)]}(ClO₄)₃ was mounted on a glass fiber and used for data collection. Crystallographic and refinement data are summarized in Table 1. The crystallographic data were collected at 173(2) K on an Enraf Nonius FR590 diffractometer using graphite-monochromated Mo Kα radiation and were processed with HKL Denzo and Scalepack, in the Departments

of Chemistry of the Universities of Helsinki, Helsinki, Finland, and Jyväskylä, Jyväskylä, Finland.¹⁶ The structure was solved by direct methods using SHELXS-97¹⁷ and was refined by full-matrix least-squares techniques against *F*² using SHELXL-97. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically, and positional parameters were refined using a riding model. Atomic scattering factors were obtained with the use of ref 18. Molecular graphics were obtained from ORTEP-3 for Windows and Mercury.¹⁹ Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 263778. These data can be obtained free of charge via clicking www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223 336033).

Synthesis of Metal Complexes. General Procedure. A solution of **L** (0.10 g, 0.37 mmol) in dichloromethane (4 mL) was added dropwise to an acetonitrile solution of M(ClO₄)₂·6H₂O (0.37 mmol, 4 mL). The resulting solution was stirred at room temperature for 2 h, and the solution was partially reduced to a volume of ca. 3 mL. Diethyl ether was infused into the solution producing polycrystalline precipitates. The products were filtered off, washed with diethyl ether, and recrystallized by diffusion of diethyl ether into acetonitrile or ethanol solutions.

{[Co(ClO₄)(H₂O)(L)][Co(H₂O)₂(L)]}(ClO₄)₃. Yield: 0.12 g, 62%. Anal. Calcd for C₁₃H₂₀N₂S₂CoCl₂O₈·CH₃CN·H₂O: C, 30.80; H, 4.30; N, 7.20; S, 10.95. Found: C, 30.70; H, 4.00; N, 6.85; S, 10.60. Conductivity (CH₃CN, 1 × 10⁻³ M): 239 μS cm⁻¹. UV (CH₃CN): λ = 499 (ε = 93), 1010 nm (15 M⁻¹ cm⁻¹). MS-ESI (*m/z*): 426.0 [Co(ClO₄)(L)]⁺. IR (KBr pellet): 3437, 3335, 3159, 2928, 1601, 1575, 1457, 1431, 1143, 1115, 1087, 923, 626 cm⁻¹. Dark red crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of carbon tetrachloride into a nitromethane solution.

[Cu(ClO₄)(L)](ClO₄). This compound was obtained by the general procedure using ethanol instead of acetonitrile to avoid formation of Cu(I) species. Yield: 0.12 g, 62%. Anal. Calcd for C₁₃H₂₀N₂S₂CuCl₂O₈·CH₃CH₂OH: C, 31.25; H, 4.55; N, 4.85; S, 11.10. Found: C, 31.10; H, 4.35; N, 4.75; S, 11.35. Conductivity (CH₃CH₂OH, 1 × 10⁻³ M): 73 μS cm⁻¹. UV (CH₃NO₂): λ = 593 nm (ε = 319 M⁻¹ cm⁻¹). MS-ESI (*m/z*): 165.5 [Cu(L)]²⁺; 430.1 [Cu(ClO₄)(L)]⁺. IR (KBr pellet): 3535, 3243, 2930, 1638, 1601, 1465, 1433, 1144, 1109, 1089, 637, 626 cm⁻¹.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.

Results and Discussion

Synthesis of Co(II) Complexes. The reaction between equimolar amounts of **L** with Co(ClO₄)₂·6H₂O in acetonitrile yielded a pink microcrystalline solid whose elemental analysis fits the formula Co(L)(ClO₄)₂(CH₃CN)(H₂O). The electronic spectrum shows a multiple band around 500 nm

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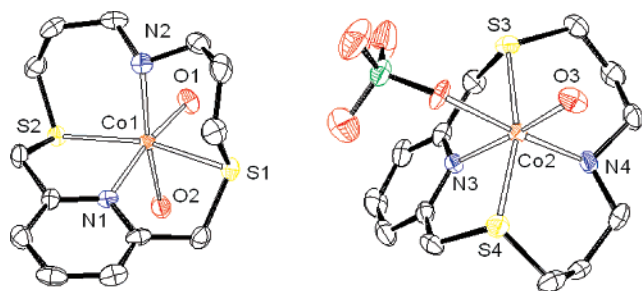


Figure 1. Displacement ellipsoid representation of both complex cations of compound $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$. Ellipsoids are shown at the 40% probability level. Noncoordinated counterions and hydrogen atoms were omitted for clarity.

and a single band with extinction coefficient around $15 \text{ M}^{-1} \text{ cm}^{-1}$ at 1010 nm , as expected for octahedral $\text{Co}(\text{II})$ complexes.²⁰ This compound behaves as a 2:1 electrolyte in acetonitrile, which indicates that perchlorates are not coordinated to metal ions. These data suggest that, at least in solution, all four donor atoms of **L** and two solvent molecules are coordinated to the metal center. In contrast, the splitting of the IR absorption corresponding to the $\nu(\text{ClO}_4^-)$ stretching vibrational band around 1100 cm^{-1} (1115 and 1087 cm^{-1}) suggests that at least one of the two perchlorate ions of each $\text{Co}(\text{II})$ ion is coordinated to the metal center in the solid state.²¹ The existence of such $\text{Co}-\text{ClO}_4$ interactions was confirmed by single-crystal X-ray diffraction analysis. The crystal structure of this compound contains the two complex cations $[\text{Co}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Co}(\text{ClO}_4)(\text{L})(\text{H}_2\text{O})]^+$. In the first one, the cobalt atom is coordinated to two oxygen atoms of water molecules and all donor atoms of one **L** molecule. The cobalt center located in the second complex cation is coordinated to one oxygen atom of a water molecule, one oxygen atom of a perchlorate anion, and all four donor atoms of a macrocyclic ligand. The structure is completed by three additional perchlorate anions without significant interactions with the above-mentioned cations. Therefore, the crystallized compound should be formulated as $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$. An ORTEP view of this structure is shown in Figure 1. Selected bond lengths and angles are summarized in Table 2.

The structure of the two complex cations is conditioned by the meridional coordination of the 2,6-bis(thiomethyl)pyridine unit, as observed in the values of the $\text{S}-\text{Co}-\text{S}$ angles ($162.63(6)$ and $164.59(6)^\circ$). In both cases, the aliphatic nitrogen is located perpendicular to the plane defined by the pyridine nitrogen and the two thioether-sulfur atoms. This geometric arrangement is achieved with the folding of the macrocycle along the line defined by the sulfur atoms, leading to a dihedral angle of $111.5(1)^\circ$ between the planes $[\text{S}(1), \text{N}(1), \text{S}(2)]$ and $[\text{S}(1), \text{N}(2), \text{S}(2)]$ of the $[\text{Co}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ cation and a dihedral angle of $94.2(3)^\circ$ between the planes $[\text{S}(3), \text{N}(3), \text{S}(4)]$ and $[\text{S}(3), \text{N}(4), \text{S}(4)]$ of the $[\text{Co}(\text{ClO}_4)(\text{L})-$

Table 2. Selected Bond Lengths (\AA) and Angles ($^\circ$) for $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$

param ^a	$[\text{Co}(\text{L})(\text{H}_2\text{O})_2]^{2+}$	$[\text{Co}(\text{ClO}_4)(\text{L})(\text{H}_2\text{O})]^+$
$\text{Co}-\text{N}(\text{o})$	2.115(5)	2.066(5)
$\text{Co}-\text{N}(\text{e})$	2.143(5)	2.120(5)
$\text{Co}-\text{O}(\text{o})$	2.081(5)	2.057(4)
$\text{Co}-\text{O}(\text{e})$	2.146(5)	2.289(4)
$\text{Co}-\text{S}(\text{o})$	2.4739(17)	2.4216(17)
$\text{Co}-\text{S}(\text{e})$	2.4318(16)	2.4564(17)
$\text{N}(\text{o})-\text{Co}-\text{N}(\text{e})$	103.61(19)	96.04(19)
$\text{N}(\text{o})-\text{Co}-\text{O}(\text{o})$	169.03(19)	170.04(19)
$\text{N}(\text{o})-\text{Co}-\text{O}(\text{e})$	87.92(18)	86.58(17)
$\text{N}(\text{e})-\text{Co}-\text{O}(\text{o})$	87.2(2)	93.3(2)
$\text{N}(\text{e})-\text{Co}-\text{O}(\text{e})$	168.47(19)	176.67(19)
$\text{S}(\text{o})-\text{Co}-\text{S}(\text{e})$	162.63(6)	164.59(6)
$\text{S}(\text{o})-\text{Co}-\text{N}(\text{o})$	81.57(14)	83.80(14)
$\text{S}(\text{o})-\text{Co}-\text{N}(\text{e})$	91.3(15)	92.39(15)
$\text{S}(\text{e})-\text{Co}-\text{N}(\text{o})$	81.12(14)	85.05(14)
$\text{S}(\text{e})-\text{Co}-\text{N}(\text{e})$	94.05(15)	99.34(15)
$\text{S}(\text{o})-\text{Co}-\text{O}(\text{o})$	96.85(15)	99.26(13)
$\text{S}(\text{o})-\text{Co}-\text{O}(\text{e})$	90.43(14)	85.84(12)
$\text{S}(\text{e})-\text{Co}-\text{O}(\text{o})$	99.89(15)	90.06(13)
$\text{S}(\text{e})-\text{Co}-\text{O}(\text{e})$	87.59(14)	82.90(12)
$\text{O}(\text{o})-\text{Co}-\text{O}(\text{e})$	81.23(19)	84.20(18)

^a Atom numbering: (o) 1 for $[\text{Co}(\text{L})(\text{H}_2\text{O})_2]^{2+}$, 3 for $[\text{Co}(\text{ClO}_4)(\text{L})(\text{H}_2\text{O})]^+$; (e) 2 for $[\text{Co}(\text{L})(\text{H}_2\text{O})_2]^{2+}$, 4 for $[\text{Co}(\text{ClO}_4)(\text{L})(\text{H}_2\text{O})]^+$.

$(\text{H}_2\text{O})]^+$ cation. The folded conformation adopted by **L** is probably preferred to avoid steric impediments between the metal center and the 14-membered macrocyclic cavity. Such folded conformation leaves the two coordination sites occupied by water molecules or perchlorate ions in a relative cis orientation. The $\text{Co}-\text{O}_{\text{water}}$ and $\text{Co}-\text{O}_{\text{perchlorate}}$ bond lengths in the $[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})]^+$ cation ($2.057(4)$ and $2.289(4) \text{ \AA}$, respectively) are close to the average distances obtained from the Cambridge Structural Database (CSD) for octahedral $\text{Co}(\text{II})$ complexes with $\text{Co}-\text{H}_2\text{O}$ or $\text{Co}-\text{ClO}_4$ bonds (2.093 and 2.290 \AA , respectively).²² One of the two $\text{Co}-\text{O}_{\text{water}}$ bond lengths of the $[\text{Co}(\text{H}_2\text{O})_2(\text{L})]^{2+}$ cation ($2.081(5)$ and $2.146(5) \text{ \AA}$) is slightly longer than the $\text{Co}-\text{O}_{\text{water}}$ average distance previously mentioned. The $\text{Co}-\text{S}$ distances in both complex cations, which range between $2.4216(17)$ and $2.4739(17) \text{ \AA}$, are similar to those found in the three reported $\text{Co}(\text{II})$ complexes containing the 2,6-bis-(thiomethyl)pyridine unit (ca. 2.471 \AA).²³ The $\text{Co}-\text{N}_{\text{pyridine}}$ ($2.066(5)$ and $2.115(5) \text{ \AA}$) and the $\text{Co}-\text{N}_{\text{aliphatic}}$ bond lengths ($2.120(5)$ and $2.143(5) \text{ \AA}$) do not significantly differ from the average distances found for related $\text{Co}(\text{II})$ complexes (2.116 and 2.253 \AA , respectively).²⁴

It is important to note that although numerous structures of transition metal complexes with 14-membered polyaza²⁵

(20) n_1 , $^4\text{T}_{1g}(\text{P}) \leftarrow ^4\text{T}_{1g}(\text{F})$ ($450\text{--}600 \text{ nm}$); n_2 , $^4\text{A}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$ ($450\text{--}600 \text{ nm}$); n_3 , $^4\text{T}_{2g}(\text{P}) \leftarrow ^4\text{T}_{1g}(\text{F})$ (around 1000 nm): Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.

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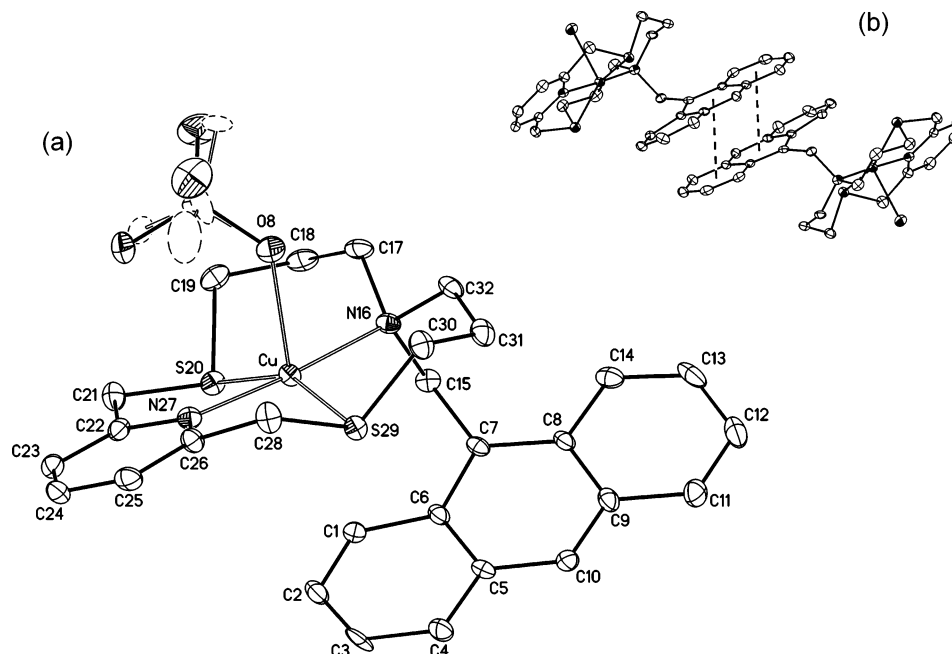


Figure 2. (a) Displacement ellipsoid representation (at the 40% probability level) of the $[\text{Cu}(\text{ClO}_4)(\text{L1})]^+$ ion, with the atom-numbering scheme adopted. Noncoordinated counterions and hydrogen atoms were omitted for clarity. (b) Perspective view of dimers of $[\text{Cu}(\text{ClO}_4)(\text{L1})]^+$ showing the $\pi \cdots \pi$ interactions. Reproduced with permission from: *Inorg. Chem.* **2005**, *44*, 8105–8115. Copyright 2005 American Chemical Society.

or oxaazamacrocycles²⁶ have already been reported, only a few transition metal complexes with 14-membered thiaazamacrocycles are reported in the literature.^{13,27} As a matter of fact, the structure of $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$ is the third one in which a Co(II) ion is coordinated to a 14-membered thiaazamacrocycle.²⁸ Another important feature of this structure is that it has a cobalt center coordinated to a perchlorate ion since, up to now, only 16 structures containing Co–ClO₄ sets have been reported in the literature.²²

Synthesis of Cu(II) Complexes. A Dark blue microcrystalline powder was isolated from the reaction of **L** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol solution. The elemental analysis of this powder fits the formula $\text{Cu}(\text{L})(\text{ClO}_4)_2(\text{CH}_3\text{CH}_2\text{OH})$. This compound behaves as a 2:1 electrolyte in ethanol which suggests that, at least in solution, the ClO₄[−] ions are not involved in the coordination of the Cu(II) ions. On the other hand, the IR spectrum of this compound (as a KBr pellet) shows the splitting of the $\nu(\text{ClO}_4^-)$ stretching vibrational band at around 1100 cm^{−1} (1109 and 1080 cm^{−1}), which indicates that, in the solid state, such ClO₄[−] ions are contributing to the coordination sphere of Cu(II).²¹ If one

takes into account the well-known ability of macrocycle **L** to act as a tetradentate ligand,^{12,13,29} the IR spectrum, and the elemental analysis, two hypotheses for the solid state can be suggested: (1) Each Cu atom is pentacoordinated by all four donor atoms of a **L** molecule and one O atom from a ClO₄[−] ion, and therefore, there is a noncoordinated ethanol molecule present in the lattice. (2) Each Cu atom is hexacoordinated by the four donor atoms of a **L** molecule, one O atom from a perchlorate ion, and another O atom (from a perchlorate ion or from an ethanol molecule). A search in the Cambridge Crystallographic Database for Cu(II) compounds containing N₂S₂X-based cores (X = ClO₄)²² revealed that all reported structures correspond to pentacoordinated Cu(II) complexes.^{13,30} It is important to emphasize that one of these reported structures corresponds to the Cu(II) complex of the closely related ligand **L1** $\{[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)\}$, in which the metal ion is pentacoordinated by the four donor atoms of the macrocyclic ligand and one O atom from a ClO₄[−] ion (see Figure 2a). These data suggest that the first hypothesis is the most likely and that this complex should be thus formulated as $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$.

EPR Experiments of Co(II) Complexes. In a purely octahedral environment, the ground state of a Co(II) ion is ⁴T_{1g}.^{31,32} This is further split by spin–orbit interaction and by lower symmetry distortions of the ligand field, resulting

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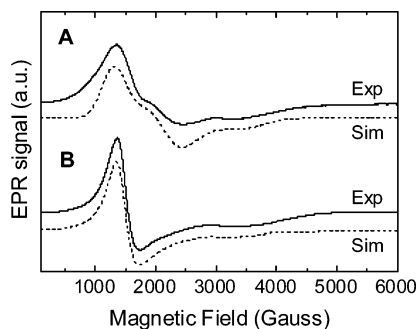


Figure 3. Experimental and simulated EPR spectra of (A) a powdered sample and (B) an acetonitrile solution of $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$ recorded at 4 K and 9.65 GHz. The EPR parameters used for simulation were (a) $g_1 = 5.20$ (300), $g_2 = 3.20$ (380), and $g_3 = 1.95$ (550) and (b) $g_1 = g_2 = 4.79$ (280), $g_3 = 2.03$ (100), and $A_3 = 100$ G. Line widths are in gauss in parentheses. A_3 corresponds to the hyperfine constant.

into two Kramers doublets. If the energy gap between the two doublets is high enough ($\gg kT$), only the ground state is expected to be substantially populated. Figure 3a shows the EPR powder spectrum of $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$. The EPR parameters obtained from simulation assuming an effective $S' = 1/2$ (see caption of Figure 3 for further details) are typical of distorted six-coordinated Co(II) ions in a high-spin ($S = 3/2$) configuration, in which the ground state corresponds to the Kramers doublet with $S = 1/2$.^{11,33,34} These parameters are similar to those found for a Co(II) compound with ligand **L1**.¹³

The powder simulation shown in Figure 3 was obtained assuming isolated Co(II) sites with identical **g** tensors. This assumption is suggested by X-ray data, which do not show any chemical path able to collapse the signals of the nonequivalent Co(II) ions of the lattice, and supported by the single-crystal EPR experiment described below. The rhombicity of the EPR powder spectrum indicates an axial ZFS with a small rhombic contribution ($E/D = 0.16$).^{33,34} Although the coordination geometries of the two different Co sites are very similar, the discrepancies observed between simulation and experimental spectra may be indicating that the **g** tensor associated with both Co(II) centers are not identical. The existence of two chemically different Co(II) ions was also observed from oriented single-crystal EPR spectroscopy with the magnetic field in the *ab*, *ac*, and *cb* crystallographic planes. As discussed above, this compound crystallizes in the orthorhombic space group $P2_1ab$ having two different Co sites/unit cell, identified as Co1 and Co2 (see Figure 1). The single-crystal EPR experiment showed two different resonances along the crystal axes, which must be associated with the two chemically different and non-symmetry related Co(II) ions present in the unit cell.³⁵ For intermediate magnetic field orientations, the EPR spectra

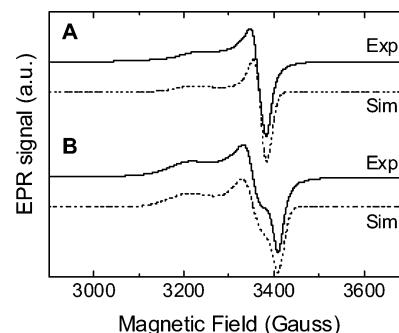


Figure 4. Experimental and simulated EPR spectra of powdered samples of (A) $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ and (B) $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$, recorded at room temperature and 9.65 GHz. EPR simulations were performed using $g_1 = g_2 = 2.043$ (26), and $g_3 = 2.145$ (80) for $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ and $g_1 = 2.025$ (26), $g_2 = 2.060$ (34), and $g_3 = 2.155$ (80) for $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$. Line widths are in gauss in parentheses.

correspond to the overlap of the four resonance lines associated with the four Co(II) sites in the unit cell. The complexity of these spectra precludes a detailed analysis of both the position of the resonance and the assignment of the signals corresponding to the different Co sites. All these experimental evidence confirms that the nonequivalent Co(II) ions are not collapsed by exchange interaction, which was a central assumption in the powder spectrum simulation.

The spectrum of a frozen acetonitrile solution of $\{[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})]\}(\text{ClO}_4)_3$ (Figure 3b) is also typical of high-spin Co(II) ions. In this case, however, the spectrum was well-simulated by assuming a single Co(II) ion having a **g** tensor with axial symmetry. This result indicates a less distorted metal environment and suggests the presence of only one type of cobalt site, which is in good agreement with the conductivity measurements.

EPR Experiments of Cu(II) Complexes. Figure 4 shows both experimental and simulated EPR spectra of powder samples of $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ and $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$. As previously reported, the EPR signal of $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ is nearly axial with *g* values $g_1 = 2.025$, $g_2 = 2.060$, and $g_3 = 2.155$ and without resolved hyperfine structure due to copper nuclear spin $I = 3/2$.¹³ Since the structure of this complex does not show any superexchange path able to collapse the signals of the nonequivalent Cu(II) ions of the unit cell, the EPR spectrum can be assumed as that corresponding to single Cu(II) ions. Weak exchange interaction mediated by π – π interactions between magnetically equivalent Cu(II) ions (see Figure 2b) was assumed to be the cause of the absence of resolved hyperfine structure. The EPR spectrum of $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ was simulated assuming an axial **g** tensor ($g_1 = g_2 = 2.043$, $g_3 = 2.145$). The axial symmetry of the powder spectrum suggests that this compound should correspond to a weakly exchanged copper system, where the *g* values are not too different from those associated with isolated Cu(II) ions.³⁶ The analogous EPR parameters found for both compounds suggest quite similar geometry of coordination for both metal sites. However, since the deviation of the **g** tensor from axial symmetry is lower in the Cu(II) complex of **L** than that in

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(35) Symmetry-related Co(II) ions give the same EPR signal along the crystal axes.

(36) Exchange-coupled copper systems almost never yield axial spectra.

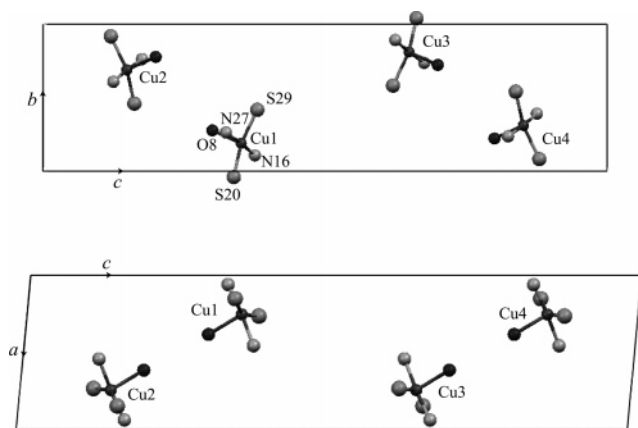


Figure 5. Projection of the unit cell of $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ containing the four Cu(II) ions and their ligands along the a -axis (upper) and b -axis (lower).

the Cu(II) complex of **L1**, a higher ligand field symmetry is expected for $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$.³⁷ Differences in the chemical composition of both compounds (absence of anthracene moiety in $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$) might be the cause of the slightly different EPR behavior.

Different results were obtained when the EPR spectrum of $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ was recorded in frozen solution (not shown). The differences between the EPR spectra in the solid state and in solution indicate that the coordination environment of the Cu(II) ion is not the same in both samples. These coordination differences were also detected when comparing the conductivity of an ethanol solution of $[\text{Cu}(\text{ClO}_4)(\text{L})](\text{ClO}_4)$ with the IR spectrum of the complex (recorded as a KBr pellet). No EPR signal was obtained from a frozen solution of $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$, because of its low solubility.

To evaluate the \mathbf{g} tensor orientation in the molecular frame, $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ was studied by single-crystal EPR spectroscopy. The unit cell of this compound contains four identical Cu(II) complex cations related by the symmetry operations of the space group $P2_1/c$ (Figure 5). Cu1 at the general position (x, y, z) is related to Cu2 by a C_{2b} rotation, as well as Cu3 to Cu4. Cu1 and Cu2 are related to Cu3 and Cu4, respectively, by an inversion center. From the magnetic point of view, this compound can be assumed as having two magnetically nonequivalent molecules/unit cell, because the Cu sites related by an inversion center are indistinguishable by EPR spectroscopy. Single-crystal EPR spectra were recorded with the magnetic field in three orthogonal crystal planes as explained in the Experimental Section. As expected, in the c^*a plane and along the b crystal axis, only one resonance line was observed, since the sites are magnetically equivalent. Two lines were observed in the ab crystal plane, which can be assigned to the Cu(II) ion pairs Cu1–Cu3 and Cu2–Cu4. Although the difference in g factors for the two magnetically nonequivalent Cu sites in this plane is very small ($\Delta g_{\text{max}}^{ab} \sim 0.04$), the single-crystal experiment has resolution enough to distinguish both lines. A similar result would be expected in the c^*b crystal plane, but only one

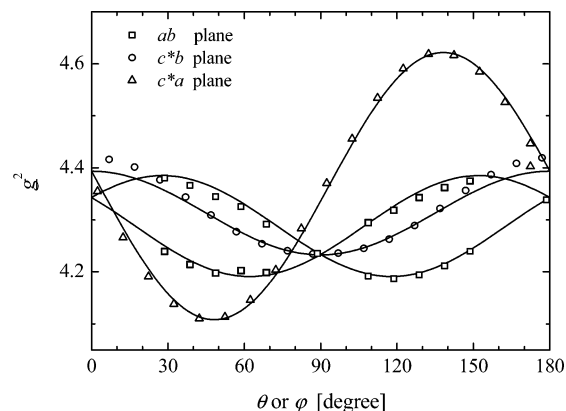


Figure 6. Angular variation of the square g -factor obtained from oriented single-crystal EPR measurements of compound $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ recorded at room temperature and at 9.77 GHz. Solid lines were calculated with the components of the \mathbf{g}^2 tensor given in Table 3.

resonance line was observed. This result indicates that the Δg for the c^*b plane is even much lower than Δg for the ab plane ($\Delta g_{\text{max}}^{c^*b} \leq 0.01$). Hence, the obtained angular variation of the g factor in the c^*b plane can be assumed, without a significant error, to be associated with any of the two nonequivalent Cu sites.

To determine the position of the resonance lines, these spectra were least-squares fitted to a Gaussian line shape for the c^*b and c^*a planes and to a sum of two normalized Gaussian lines in the case of the ab plane, except where the resolution was not good enough to discriminate between the two lines. Similar results and fitting quality are obtained when using Lorentzian line shapes, indicating that the resonance lines represent a compromise between the two line shapes, which is typical of exchange-coupled extended systems.³⁸ Figure 6 shows the angular variation of the g factor for the two rotated Cu sites as a function of the magnetic field orientation. The data for each Cu site were least-squares fitted to a second rank tensor $\mathbf{g}^2(\theta, \phi) = \mathbf{h} \cdot \mathbf{g} \cdot \mathbf{g} \cdot \mathbf{h}$, in which \mathbf{h} ($\mathbf{h} = \sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta$) is the magnetic field orientation and \mathbf{g} is the molecular \mathbf{g} tensor of the Cu(II) ion in the crystal lattice. The results are given in Table 3 and were used to obtain the solid lines in Figure 6. The overall symmetry of the evaluated \mathbf{g} tensors follows the symmetry determined by the space group of this compound. The eigenvalues and the eigenvectors obtained from the analysis of the data in Figure 6 are also included in Table 3.

The eigenvalues are similar to those obtained from EPR simulation of the powdered samples, which confirms that this spectrum corresponds to that of single Cu(II) ions, in which the hyperfine interaction is collapsed by exchange interactions between equivalent ions. Because of the monoclinic symmetry of the lattice of $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$, there are two possible orientations for the molecular \mathbf{g} tensor, indicated as assignments I and II in Table 3 and Figure 7. The eigenvector of the highest eigenvalue (g_3) is nearer along the normal to the copper equatorial ligands for assignment I ($\angle g_3\text{-normal} = 12.64^\circ$) than for assignment II ($\angle g_3\text{-normal}$

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Table 3. Values of the Components of the g^2 Tensor of $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$, Obtained by Least-Squares Analyses of the Data at 9.77 GHz^a

Components of g^2		
$(g^2)_{xx} = 4.344(5)$	$(g^2)_{xy} = 0.082(5)$	
$(g^2)_{yy} = 4.235(4)$	$(g^2)_{zx} = 0.255(5)$	
$(g^2)_{zz} = 4.392(4)$	$(g^2)_{zy} = 0.000(5)$	
Eigenvalues		
$(g^2)_1 = 4.085(6)$	$(g^2)_3 = 4.632(5)$	
$(g^2)_2 = 4.251(5)$		
Eigenvectors: Assignment I		
$a_1 = [0.708(6), 0.39(2), 0.59(1)]$	$a_3 = [0.677(4), -0.14(1), -0.723(4)]$	
$a_2 = [0.20(1), -0.91(1), 0.36(2)]$		
Eigenvectors: Assignment II		
$a_1 = [-0.708(6), 0.39(2), -0.59(1)]$	$a_3 = [0.677(4), 0.14(1), -0.723(4)]$	
$a_2 = [0.20(1), 0.91(1), 0.36(2)]$		

^a $(g^2)_1$, $(g^2)_2$, and $(g^2)_3$ and a_1 , a_2 , and a_3 are the eigenvalues and eigenvectors of the g^2 tensor in the $xyz = abc^*$ coordinates system ($c^* = a \times b$). The two possible orientations for the molecular g tensor are indicated as assignments I and II.

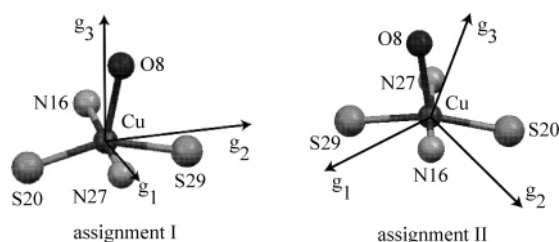


Figure 7. Two possible orientations of the principal axes of the g tensor for the Cu(II) site in $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$. The direction cosines referred to the abc^* crystal axes are given in Table 3.

$= 28.28^\circ$). The remaining two axes for the g tensor are approximately lying along the bonds for assignment I and between the bonds for assignment II.

Both the departure from axiality and the orientation of the g tensor can be rationalized in terms of the model of Hitchman et al.³⁷ In their work, it is shown that when the ligand-field component acting along the ground-state orbital directions ($d_{x^2-y^2}$ in D_{4h} symmetry) turns asymmetric by lowering the symmetry to D_{2h} , an anisotropy in g_{\perp} is produced mainly by a small admixture of the $|3z^2 - r^2\rangle$ orbital into the ground state and to a lesser extent by the different energies of the $|xz\rangle$ and $|yz\rangle$ excited-state orbitals. These ideas were tested by studying a series of copper–amino acid complexes containing N2O2 equatorial ligands in trans and cis configurations, which showed that the directions of g_{\perp} are along the bonds for copper complexes in trans configurations whereas between the bonds for the cis configurations.³⁹ Taking into account these results and

the fact that the g_3 eigenvector is closer to the axial direction, we conclude that assignment I is the most likely orientation of the g tensor for $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$. The important observed anisotropy in g_{\perp} strongly suggests this is produced by an small admixture of d_{x^2} orbital into the ground state, which determines that the g_{\perp} directions lie nearly along the bonds. However, as the true symmetry in $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ around the copper centers is even lower than D_{2h} , a nonvanishing participation of the d_{xy} , d_{xz} , and d_{yz} symmetry orbitals into the ground state may be expected.

Conclusions

New Co(II) and Cu(II) containing ligands 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L**) and 7-(9-anthracenylmethyl)-3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L1**) have been successfully synthesized and characterized. Single-crystal X-ray structural data for the Co(II) compound show two different cobalt sites coordinated to all the donor atoms of one macrocyclic unit and two oxygen atoms. X-band EPR measurements of polycrystalline samples performed on the compound $[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})](\text{ClO}_4)_3$ indicate high-spin Co(II) ion ($S = 3/2$) in an axially distorted environment. $[\text{Cu}(\text{ClO}_4)(\text{L1})](\text{ClO}_4)$ was studied by single-crystal EPR spectroscopy. Structural and EPR results allow us to assign the axes of the g tensor along the Cu–ligand bonds, with the eigenvector of the highest eigenvalue nearly along the normal to the copper equatorial ligands.

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Supporting Information Available: X-ray crystallographic data in CIF format for $[\text{Co}(\text{ClO}_4)(\text{H}_2\text{O})(\text{L})][\text{Co}(\text{H}_2\text{O})_2(\text{L})](\text{ClO}_4)_3$, CSD searches for octahedral Co(II) complexes with Co– ClO_4 and Co– H_2O bonds and for Cu(II) complexes containing $\text{N}_2\text{S}_2\text{X}$ -based cores ($\text{X} = \text{ClO}_4$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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