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[20] The amphiphilic block copolymer (2 g) is dissolved in tetramethylorthosilicate (TMOS, 4 g), which is then hydrolyzed by adding dilute hydrochloric acid (pH 2, 2 g). Initially, an isotropic mixture is obtained. Methanol is removed by evaporation in vacuo (25 Torr, 30°C), upon which the reaction mixture turns viscous and birefringent. The subsequent sol–gel process is carried out at room temperature (50°C for SE30/30) in an open flask. After 12 h the liquid crystalline mixtures are solid and, after extraction of a major portion of the template with acetone for 24 h, are calcined at 550°C (12 h under nitrogen, 12 h under oxygen).
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[25] The X-ray data were fitted with Lorentzian functions. The normalized peak positions for the first three peaks are 1.00, 1.73, and 2.00, which indicates a hexagonal symmetry of the packing.

Why Does the Active Form of Galactose Oxidase Possess a Diamagnetic Ground State?[**]

Jochen Müller, Thomas Weyhermüller, Eckhard Bill, Peter Hildebrandt, Linda Ould-Moussa, Thorsten Glaser, and Karl Wieghardt[*]

Dedicated to Professor Gottfried Huttner
on the occasion of his 60th birthday

The fungal enzyme galactose oxidase (GO) contains in its active site a square-pyramidally coordinated Cu^{II} ion (d^9) with an O-bound tyrosyl radical (Tyr 272) in the equatorial plane (see Figure 1). This catalytically active copper(II)–tyrosyl radical form is EPR-silent and has been proposed to possess a diamagnetic ground state ($S = 0$).[1a] The unpaired electron in the $d_{x^2-y^2}$ magnetic orbital of the Cu^{II} ion is then intramolecularly *antiferromagnetically* coupled to the electron of in the half-occupied π orbital of the tyrosyl radical. This is somewhat surprising, because in all known Cu^{II}–semiquinonate complexes this intramolecular exchange coupling is *ferromagnetic*, yielding an $S = 1$ ground state.[2] What is the mechanism of the exchange coupling in GO?

A catalytically inactive form of GO (pH = 4.5) containing a reduced Cu^{II}-tyrosinate moiety has been characterized by X-ray crystallography (Figure 1).[3] It has been shown that the conformation of the coordinated Tyr 272 ligand is fixed by π stacking with the tryptophane residue Trp 290. It is assumed that one-electron oxidation of Tyr 272 yielding the coordinated tyrosyl ligand does not change the conformation of the phenyl ring or the Cu-O-C bond angle significantly.

Recently Tolman et al.[4] and we[5] have reported some low molecular weight, structurally characterized Cu^{II}–phenolate complexes that can be chemically or electrochemically oxidized to generate relatively stable Cu^{II}-phenoxyl species.[6] These complexes are EPR-silent; they possess a diamagnetic ($S = 0$) ground state.[7] In these compounds the coordinated phenolate ligands are connected to the coordinated macrocycle 1,4,7-triazacyclononane (Figure 2); a six-membered chelate ring $\overline{\text{Cu}^{\text{II}}\text{NCCCO}}$ is formed. It is then natural to assume that the conformation of the chelate ring does not change upon one-electron oxidation of the phenolate to a coordinated phenoxyl.

A qualitative analysis of the relative orientations of the magnetic orbitals of the Cu^{II} ion ($d_{x^2-y^2}$) and of the phenoxyl radical (the half-occupied π orbital) reveals that they are strictly orthogonal at an Cu^{II}-O-C bond angle α of 180°, irrespective of the dihedral angle β between the x,y plane at the Cu^{II} ion and the phenyl ring of the radical ligand (Figure 3). According to the Goodenough–Kanamori rules

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[*] Prof. Dr. K. Wieghardt, Dipl.-Chem. J. Müller, Dr. T. Weyhermüller, Dr. E. Bill, Dr. P. Hildebrandt, Dr. L. Ould-Moussa,
Dipl.-Chem. T. Glaser
Max-Planck-Institut für Strahlenchemie
Stiftstrasse 34–36, D-45470 Mülheim an der Ruhr (Germany)
Fax: +(49)208-306-3952
E-mail: wieghardt@mpi-muelheim.mpg.de

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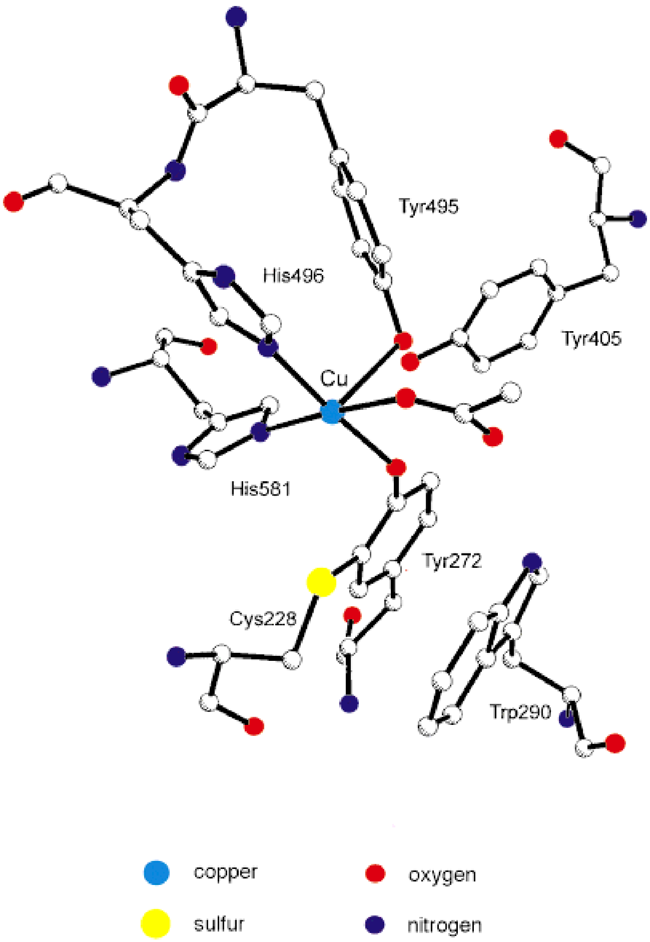
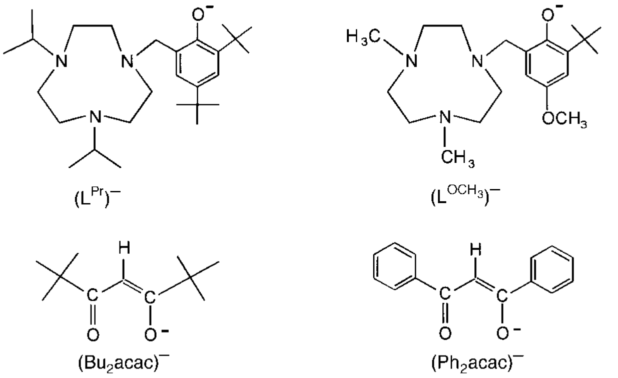


Figure 1. Schematic representation of the active site of galactose oxidase (pH = 4.5).[3]



$[L^{Pr}Cu^{II}Cl]$	1[4]
$[L^{OCH_3}CuCl]$	2
$[L^{OCH_3}Cu^{II}(Ph_2acac)]$	3
$[L^{OCH_3}Cu^{II}(Bu_2acac)]$	4

Figure 2. Ligands and complexes.

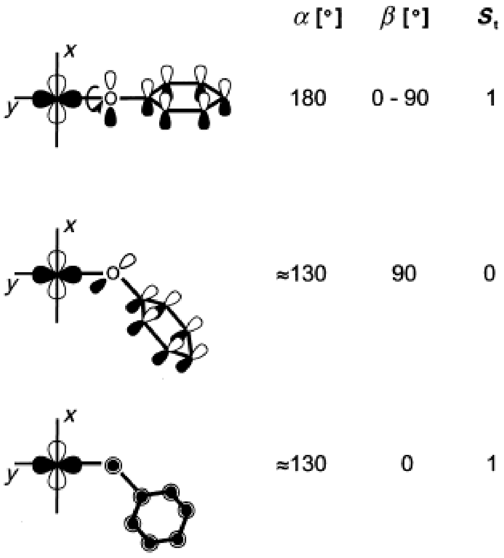


Figure 3. Relative orientations of the magnetic orbitals of the Cu^{II} ion ($d_{x^2-y^2}$) in the x,y plane relative to that of the half-occupied π orbital of the phenoxyl radical. α: Cu-O-C bond angle. β: dihedral angle between the x,y plane and the plane of the phenyl ring of the coordinated phenoxyl. S_t: expected electronic ground state.

for exchange coupling a ferromagnetic coupling will then stabilize the triplet ground state ($S = 1$). If the observed bond angle α is in the range 125–135°, the magnitude of the dihedral angle β determines the multiplicity of the electronic ground state: at $\beta = 0°$ the magnetic orbitals are again strictly orthogonal and $S = 1$ is the ground state, but at $\beta \approx 90°$ the significant overlap between the magnetic orbitals stabilizes a singlet ground state ($S = 0$). In GO the bond angle α is about 129° and $\beta \approx 75°$, which according to the above analysis results in an $S = 0$ ground state—as is observed.

We were able experimentally to corroborate the above analysis as follows: We synthesized the mononuclear complexes **2**, **3**, and **4** (Figure 2) all of which contain the tetradentate macrocyclic anion $(L^{OCH_3})^-$. Complex **2** is five-coordinate; its structure is proposed to be very similar to that of **1**, which has been analyzed by X-ray crystallography.[4]

In **3** and **4** the chloro ligand is replaced by the didentate β-diketonates Ph_2acac^- and Bu_2acac^-, which enforces the coordination number 6 at the Cu^{II} ions. Figure 4 displays the structure of **3**.[8] The *cis*-$Cu^{II}N_3O_3$ polyhedron exhibits a marked tetragonal Jahn–Teller distortion: The Cu–N and Cu–O bond lengths of the N(2)-Cu(1)-O(2) axis (z axis) are both longer than the corresponding lengths in x and y direction. The unpaired electron occupies a $d_{x^2-y^2}$ metal orbital as in the square-pyramidal Cu^{II} ion in **2**. This has been corroborated by the EPR spectra of these Cu^{II} complexes.

Cyclic voltammograms of **2**, **3**, and **4** recorded in CH_2Cl_2 (20°C, 0.10 M $[(n\text{Bu})_4\text{N}]\text{PF}_6$) exhibit in the potential range from 0.2 to −1.2 V vs. ferrocenium/ferrocene (Fc^+/Fc) one reversible one-electron oxidation ($E_{1/2}$ vs Fc^+/Fc for **2**: −0.015 V; **3**: −0.33 V; **4**: −0.42 V). Figure 5 shows the UV/Vis spectra of **4** and **2**, as well as their electrochemically one-electron oxidized forms $[\mathbf{4}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$. The intense absorption maxima of $[\mathbf{4}]^{\bullet+}$ at 391, 411, and 477 nm are characteristic of the phenoxyl radical. The resonance Raman (RR) spectrum of $[\mathbf{4}]^{\bullet+}$ in CH_2Cl_2 ($\lambda_{exc} = 413$ nm) displays the typical strong C–O phenoxyl stretching mode at 1509 cm^{-1} and a weaker C=C vibration at 1602 cm^{-1}.[5] The energy difference Δ of 107 cm^{-1} between these two modes conclusively demonstrates that the phenoxyl radical is O-bound to the Cu^{II} ion.[9]

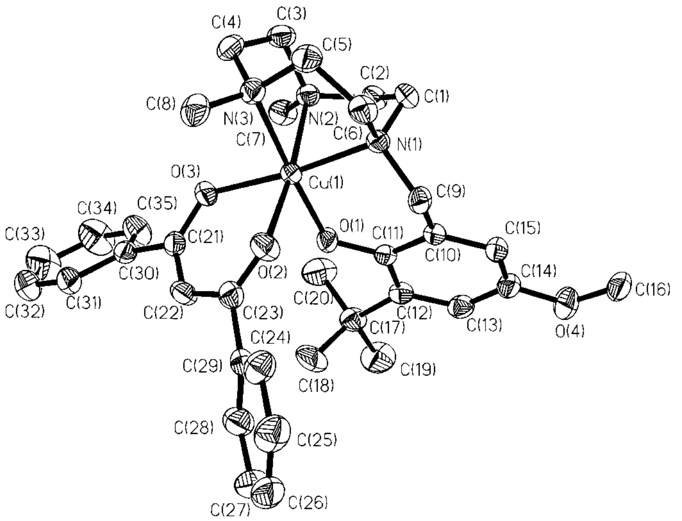


Figure 4. Structure of **3** in the crystal. Selected bond lengths [Å] and angles [°]: Cu(1)-O(1) 1.914(2), Cu(1)-O(2) 2.330(2), Cu(1)-O(3) 1.994(2), Cu(1)-N(1) 2.04782), Cu(1)-N(2) 2.333(2), Cu(1)-N(3) 2.125(2), O(1)-C(11) 1.325(3), O(3)-C(21) 1.268(3), O(2)-C(23) 1.243(3), C(21)-C(22), 1.392(4), C(22)-C(23) 1.421(4); Cu(1)-O81)-C(11) 129.2(2), N(3)-Cu(1)-O(1) 176.9(1), O(3)-Cu(1)-N(1) 173.7(1), O(2)-Cu(1)-N(2) 172.0(1).

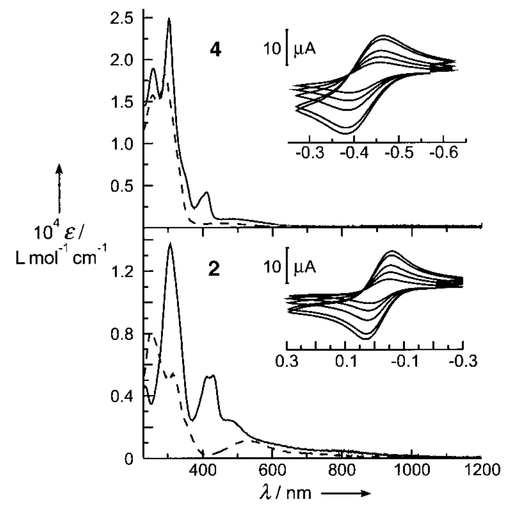


Figure 5. UV/Vis spectra (CH_2Cl_2) of **4** and **2** (broken lines) and of the electrochemically generated oxidized forms $[\mathbf{4}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$ (solid lines). The insets show the cyclic voltammograms of **4** and **2** in CH_2Cl_2 (0.10 M $[(n\mathrm{Bu})_4\mathrm{N}]\mathrm{PF_6}$) at different scan rates (50-500 $\mathrm{mV\,s^{-1}}$).

This difference Δ is only 79 $\mathrm{cm^{-1}}$ for the uncoordinated free 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical.[10] Very similar UV/Vis and RR spectra have been obtained for the radical complexes $[\mathbf{2}]^{\bullet+}$ and $[\mathbf{3}]^{\bullet+}$. Compounds $[\mathbf{2}]^{\bullet+}$, $[\mathbf{3}]^{\bullet+}$, and $[\mathbf{4}]^{\bullet+}$ contain the same coordinated radical ligand $(\mathrm{L^{OCH_3}})^{\bullet}$.

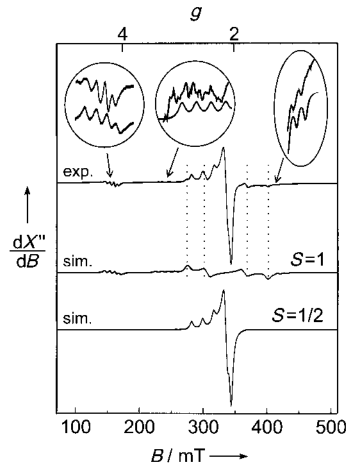


Figure 6. X-band EPR spectrum of electrochemically generated $[\mathbf{3}]^{\bullet+}$ in CH_2Cl_2 (0.10 M $[(n\mathrm{Bu})_4\mathrm{N}](\mathrm{PF_6})$) at 16 K. Conditions: frequency 9.6463 GHz, 100.6 mW; modulation amplitude 19.7 G, modulation frequency 100 kHz. For details of the simulations see ref. [11]. In the enlarged parts of the spectra the upper line represents the experimental data and the lower line a simulation.

We then recorded the X-band EPR spectra of the electrochemically generated radical species $[\mathbf{2}]^{\bullet+}$, $[\mathbf{3}]^{\bullet+}$, and $[\mathbf{4}]^{\bullet+}$ in frozen CH_2Cl_2 solution in the temperature range 4-60 K. Solutions of $[\mathbf{2}]^{\bullet+}$ displayed no signal with the exception of a weak signal of **2** (<4%). This has also been reported by Tolman et al.[4] for $[\mathbf{1}]^{\bullet+}$. We conclude that both $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$ containing a five-coordinate $\mathrm{Cu^{II}}$ ion possess a diamagnetic ground state ($S=0$). In contrast, frozen solutions of $[\mathbf{3}]^{\bullet+}$ and $[\mathbf{4}]^{\bullet+}$ are EPR-active. Figure 6 shows the spectrum of $[\mathbf{3}]^{\bullet+}$. A typical triplet spectrum with hyperfine structure is observed in addition to a weak signal at $g \approx 2.0$ due to a mononuclear $\mathrm{Cu^{II}}$ successor species (decomposition?). From the temperature dependence of the triplet spectrum a ferromagnetic coupling constant of $J = 16 \pm 3\ \mathrm{cm^{-1}}$ ($\mathscr{H} = -2J S_1 S_2$; $S_1 = S_2 = 1/2$) was established. The spectrum of $[\mathbf{4}]^{\bullet+}$ is similar, but the hyperfine structure was not resolved.

These spectroscopic results reveal that $[\mathbf{2}]^{\bullet+}$ possesses an (S=0) ground state, whereas $[\mathbf{3}]^{\bullet+}$ and $[\mathbf{4}]^{\bullet+}$ have an (S=1) ground state, although in all three species the same radical ligand $(\mathrm{L^{OCH_3}})^{\bullet}$ is coordinated to a $\mathrm{Cu^{II}}$ ion.

A comparison of the bond angle α and the dihedral angle β in five-coordinate **1**[4] with the corresponding angles in six-coordinate **3** shows that increasing the coordination number from 5 to 6 does not change α significantly (125.2° in **1** vs. 129.2° in **3**), whereas β decreases by nearly 10° from 27.4° in **1** to 17.6° in **3**. This structural change induces the change of the sign of the exchange coupling from antiferromagnetic in $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$ to ferromagnetic in $[\mathbf{3}]^{\bullet+}$ and $[\mathbf{4}]^{\bullet+}$. This is in excellent qualitative agreement with the above analysis of the orientation of the magnetic orbitals (Figure 3).

Experimental Section

All new compounds yielded correct C, H, N analyses and mass spectra. The ligand $\mathrm{L^{OCH_3}H}$ as well as $\mathrm{Na(L^{OCH_3})}$ was synthesized according to published procedures.[9]

2: To a solution of $\mathrm{Na(L^{OCH_3})}$ (0.37 g, 1.0 mmol) in tetrahydrofuran/*n*-pentane mixture (30/10 mL) was added dehydrated $CuCl_2$ (0.134 g; 1.0 mmol). After stirring for 1 h at 20°C the volume of the reaction mixture was reduced by rotary evaporation to yield microcrystalline, violet **2**; yield 0.21 g (47%).

3: A solution of $\mathrm{Na(L^{OCH_3})}$ (0.37 g, 1.0 mmol) and $[\mathrm{Cu^I(NCCH_3)_4}](\mathrm{BF_4})$ (0.32 g, 1.0 mmol) in dry CH_3OH (30 mL) was stirred at 20°C for 20 min in the presence of air. To the deep violet solution was added $\mathrm{K[Ph_2acac]}$ (0.26 g, 1.0 mmol). Within a few minutes a brown-green precipitate of **3** formed. Recrystallization from CH_2Cl_2/CH_3CN (1/1) afforded single crystals suitable for X-ray crystallography; yield 0.28 g (44%).

4: A solution of $\mathrm{Na(L^{OCH_3})}$ (0.37 g, 1.0 mmol) and $\mathrm{Cu^ICl}$ (0.099 g, 1.0 mmol) in dry CH_3OH (30 mL) was stirred in the presence of air for 20 min. To the clear brown solution was added K[Bu_2acac] (0.22 g, 1.0 mmol), and stirring was continued for 10 min. Dropwise addition of H_2O (5 mL) and filtration initiated the precipitation of brown-green crystals of **4** within 5 h; yield 0.31 g (52 %).

Physical data of complexes: UV/Vis (CH_2Cl_2): λ_{max} nm (ε[L mol^{-1} cm^{-1}]): **2**: 252 (8.1×10^3), 315 (5.3×10^3), 532 (1.2×10^3); **3**: 254 (2.71×10^4), 334 (1.67×10^4), 358 (1.60×10^4); **4**: 256 (1.6×10^4), 293 (1.8×10^4), 451(500). [**2**]$^{\cdot+}$: 236 (4.5×10^3), 308 (1.4×10^4), 413 (5.1×10^3), 431 (5.2×10^3), 485 (2.4×10^3); [**3**]$^{\cdot+}$: 270 (2.6×10^4), 304 (2.4×10^4), 352 (2.2×10^4), 412 (6.1×10^3); [**4**]$^{\cdot+}$: 259 (1.9×10^4), 303 (2.5×10^4), 347sh (6.4×10^3), 391 (3.2×10^3), 411 (4.0×10^3), 477(990).

The radical complexes [**2**]$^{\cdot+}$, [**3**]$^{\cdot+}$, and [**4**]$^{\cdot+}$ were generated in CH_2Cl_2 solution (0.10 M [$(n\mathrm{Bu})_4$N]PF_6) by coulometry. X-Band EPR spectra (CH_2Cl_2, 10 K, 9.45 GHz): g_x, g_y, g_z ($A_x = A_y$, A_z [10^{-4} cm^{-1}]): **2**: 2.05, 2.05, 2.24 (20, 180); **3**: 2.05, 2.06, 2.26 (21.7, 176); **4**: 2.06, 2.07, 2.25 (0, 175).

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[7] The complex described in ref. [6a] is an exception. It has the phenoxyl radical in apical position of the Cu^{II} square pyramid. An (S=1) ground state has been proposed.

[8] X-ray structure analysis of **3**: Brown-green crystal ($0.42\times0.60\times0.49$ nm); $C_{35}H_{45}CuN_3O_4$, $M_r = 635.3$, monoclinic, space group $P2_1/c$, $a = 15.407(3)$, $b = 11.490(2)$, $c = 18.438(4)$ Å, $\beta = 101.69(3)°$, $V = 3196(1)$ Å^3, $Z = 4$ at 293(2) K; $\rho_{calcd} = 1.32$ g cm^{-3}; $\mu_{Mo} = 0.726$ mm^{-1}, semiempirical absorption correction. Full-matrix least-squares refinement based on F with 6083 reflections with [$I > 2\sigma(I)$] and 388 variables, final R values: $R(F) = 0.037$ and $wR(F) = 0.091$. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer. The crystallographic data were deposited as supplementary publication no. CCDC-100759 at the Cambridge Crystallographic Data Centre. Copies of the data are available from CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] In the first-derivative representation (dX''/dB) of the EPR spectrum (Figure 6) an apparently dominant signal of a Cu^{II} compound ($S = 1/2$) is detected; its intensity, however, represents only 10 % of the doubly integrated total signal. In a broad field range the oxidation product [**3**]$^{\cdot+}$ displays typical resonances of a triplet spectrum with small zero-field splitting ($D < h\nu$) as is observed for spin pairs ($S_1 = S_2 = 1/2$). $\Delta m = 1$ signals at $g < 2$ (350 – 430 mT) are clearly detected, as well as the typical half-field transitions with $\Delta m = 2$ at $g = 4$, which display a clearly resolved Cu hyperfine splitting ($I = 3/2$). The spectrum was simulated with a spin Hamiltonian for an effective spin $S = 1$ (strong coupling case) and parameters $D = 0.086$ cm^{-1}, $E/D = 0.13$, $g = (2.034, 2.021, 2.10)$ and $\mathbf{A} = (20, 20, 100)\times10^{-4}$ cm^{-1}. For the local spin of the Cu^{II} ion ($S = 1/2$) we obtained $\boldsymbol{a}_{\mathbf{Cu}} = (40, 40, 200)\times10^{-4}$ cm^{-1}, $\boldsymbol{g}_{\mathbf{Cu}} = (2.07, 2.04, 2.20)$ by using the usual spin projection technique. These values are similar to those obtained for the Cu^{II} ion in **3**. Since the signals are observed down to 4 K, the spin triplet is the ground state of [**3**]$^{\cdot+}$, owing to an intramolecular ferromagnetic coupling. The splitting energy $2J$ between the triplet and (EPR-silent) singlet has been determined from the temperature dependence of the intensities(IT vs. T) by a fitting procedure to the Boltzmann function $IT = \mathrm{const.}(1 + \exp(2J/kT)^{-1})$ in the temperature range 4 – 60 K. For I the peak-to-peak amplitudes of the measured derivative spectra at $g = 4$ were used, because the resonances are not perturbed by signals of the Cu^{II} impurity.

Synthesis and Characterization of the First Double-Bridged Tetraselenafulvalenophanes[**]

Kazuo Takimiya, Akinobu Oharuda,
Atsushi Morikami, Yoshio Aso, and Tetsuo Otsubo[*]

Since the discovery of the tetrathiafulvalene/tetracyano-*p*-quinodimethane complex (TTF – TCNQ) as the first low-dimensional organic metal,[1] TTF derivatives with modified frameworks have been examined in order to develop yet more superior organic conductors.[2] One of the basic modifications is dimerization of TTF, which makes it possible to prepare charge-transfer complexes of given stoichiometry.[3] To date, a variety of dimeric TTFs have been thus synthesized and characterized.[4] Among them, tetrathiafulvalenophanes (TTF phanes) are of current interest, because in such sophisticated systems the two TTF units can adopt a unique sandwich structure and interact strongly with each other.[5, 6] We have recently found that the double-layered TTF phanes **1** are especially good electron donors, forming highly conductive radical cation salts. The high conductivities are induced by strong intra- and intermolecular nonbonding interactions between the sulfur atoms incorporated in the TTF moieties.[6] Since nonbonding interactions between selenium atoms are generally more effective than those of sulfur, tetraselenaful-

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[*] Prof. Dr. T. Otsubo, Dr. K. Takimiya, A. Oharuda, A. Morikami, Prof. Dr. Y. Aso
Department of Applied Chemistry
Faculty of Engineering, Hiroshima University
Kagamiyama, Higashi-Hiroshima 739 (Japan)
Fax: (+81) 824-22-7191
E-mail: otsubo@ipc.hiroshima-u.ac.jp

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