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# Modified 1,4-hydroquinone ligands bridging Cu^II ions − Building blocks for a new class of quantum magnets

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## Abstract

A series of low-dimensional quantum-spin systems, including isolated Cu^II dimers, various coupled Cu^II-dimer systems and a 1-D uniform $S = 1/2$ Heisenberg antiferromagnet has been synthesized. All materials are based on hydroquinone-derived linkers connecting Cu^II ions carrying a spin of $S = 1/2$. Magnetic measurements covering wide ranges of temperature 0.06 K $\leq T \leq$ 300 K and magnetic fields $B \leq$ 50 T reveal an antiferromagnetic coupling constant $J$ of moderate strength for all systems. Electron-spin resonance measurements over wide frequency ranges have been used to determine the local coordination environment of the Cu^II centers. The distinct magnetic properties of these materials along with their flexibility against chemical modifications make them excellent model systems for exploring fundamental aspects of quantum magnetism. *To cite this article: B. Wolf et al., C. R. Chimie 10 (2007).*
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*Keywords:* Cu coordination polymer; Low-dimensional spin systems

## 1. Introduction

In the course of an interdisciplinary research program aimed at the synthesis of new classes of molecule-based quantum magnets − enabling their fundamental physical properties to be explored systematically upon variations of physical or chemical parameters − novel Cu^II-containing coordination compounds have been prepared based on hydroquinone-derived linkers. It has been shown that this class of bridging ligands is able to mediate a magnetic exchange between Cu^II ions of moderate strength, i.e. of the order of 10 K [1]. Most importantly, the hydroquinone linker can be chemically modified in a way that influences the coordination geometry of the Cu^II ions while keeping the magnetic exchange at a moderate strength. We were able to synthesize a whole series of low-dimensional quantum-spin
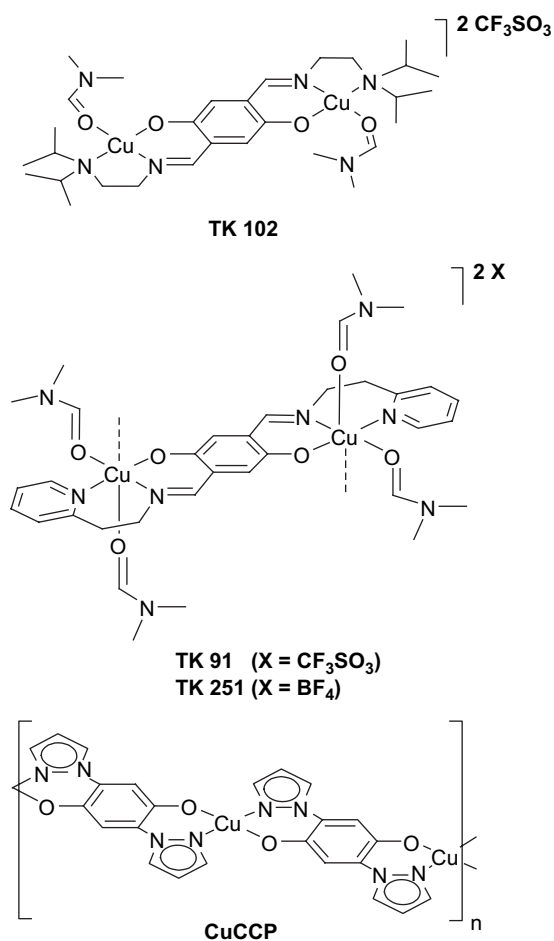
Fig. 1. Molecular units of the modified 1,4-hydroquinone-based new quantum magnets: the isolated Cu$^{II}$-dimer compound *TK 102*, coupled-dimer systems *TK 91/TK 251* and with Cu$^{II}$-2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene (*CuCCP*), a 1-D uniform antiferromagnetic $S = 1/2$ Heisenberg spin chain.

systems, cf. Fig. 1, including an isolated Cu$^{II}$ dimer (*TK 102*), coupled-dimer systems (*TK 91/TK 251*), and with Cu$^{II}$-2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene (*CuCCP*), a 1-D uniform antiferromagnetic $S = 1/2$ Heisenberg spin chain system. For the latter material we have performed experiments across the saturation field $g\mu_B B_S = 2|J|$ which marks, at $T = 0$, the endpoint of a quantum-critical line in the $B–T$ plane. It has been found that crossing $B_S$ is accompanied by a distinct magnetocaloric effect. In addition, a pronounced acoustic anomaly has been observed close to $B_S$ and identified as a generic property of the uniform antiferromagnetic $S = 1/2$ Heisenberg chain with a finite spin–lattice coupling [2]. The focus of the present work lies on a comparison of the magnetic properties of *TK 91*, *TK 102*, *TK 251* and

*CuCCP* and on an assessment of structure/property relationships; syntheses and details of the X-ray crystal structure analyses are reported elsewhere [3].

## 2. Structural aspects

In the isolated-dimer compound *TK 102*, the Cu$^{II}$ ions have a distorted square-planar coordination geometry. Each Cu$^{II}$ ion is shielded by isopropyl groups to prevent a coordination number larger than 4. Two Cu$^{II}$ ions are antiferromagnetically coupled creating a dimer with a singlet ground state. The isopropyl groups of the *TK 102* molecule are marked in light blue in Fig. 2. Also shown in Fig. 2 is one *DMF* molecule which is part of the Cu$^{II}$-coordination sphere (light orange area). *DMF* has been used as the solvent during sample preparation. The complex cations and their $O_3SCF_3$ anions are connected by weak hydrogen bonds. There are five intermolecular C–H···O contacts with H···O distances between 2.56 Å and 2.68 Å and two intermolecular C–H···F contacts with H···F distances of 2.65 Å and 2.67 Å.

The crystal structure of the $O_3SCF_3$ salt *TK 91* is rather similar to the structure of the corresponding $BF_4$ salt *TK 251*. In both compounds, the Cu$^{II}$ ions are bridged by the same hydroquinone linker to form Cu$^{II}$ dimers. In contrast to *TK 102* and as a result of the sterically less demanding hydroquinone sidearms, the Cu$^{II}$ ions in *TK 91* and *TK 251* possess a distorted octahedral coordination geometry. As shown in Fig. 2, the equatorial plane is spanned by the atoms N1, N2, O1, and O2.
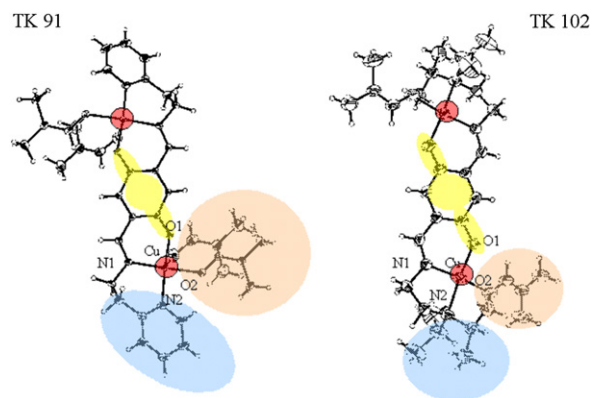


Fig. 2. Copper dimers in the coupled-dimer system *TK 91* and in the isolated-dimer compound *TK 102*. The Cu$^{II}$ ions are indicated by the red circles and the core of the hydroquinone linkers is shown in yellow. Due to the chemical modification (light blue areas) of the hydroquinone linkers the Cu coordination and local environment of the Cu$^{II}$ ions are different in the two compounds. The light orange areas indicate *DMF* molecules coordinated at the Cu$^{II}$ ions. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

In addition, there are two long axial Cu—O bonds: a Cu—O3 (*DMF*) bond of 2.565(2) Å and a Cu—O1 bond of 2.434(1) Å to a neighboring dimer (not shown in Fig. 2). Again, the two *DMF* molecules in the Cu$^{II}$-coordination sphere of *TK 91* are marked in light orange.

As a result of interdimer Cu—O1 contacts, *TK 91* establishes a polymeric structure along the crystallographic *a*-axis corresponding to the needle axis of the crystal. The same is true for the BF$_4$ salt *TK 251*. A picture of a high-quality single crystal is shown in the inset of Fig. 5. At first glance, both systems (*TK 91*, *TK 251*) seem to be dimerized spin chains. However, in both compounds, the cations and anions are connected by a large number of intermolecular C—H···O and C—H···F hydrogen bonds. In *TK 91*, there are 13 different C—H···O contacts with H···O distances between 2.51 Å and 2.75 Å and three different C—H···F contacts with H···F distances between 2.56 Å and 2.75 Å, whereas in *TK 251* there are 12 different C—H···F contacts with H···F distances between 2.34 Å and 2.75 Å.

In *CuCCP*, the hydroquinone core of the bridging ligand has two chelating pyrazolyl anchor groups as shown in Fig. 1. *CuCCP* was obtained as a microcrystalline material. Its crystal structure was determined by high-resolution X-ray powder diffraction using the method of simulated annealing [4]. The system has triclinic symmetry with a one formula unit, i.e. one Cu$^{II}$ ion per unit cell. In the solid state, *CuCCP* forms 1-D coordination polymers along the crystallographic *c*-axis and features Cu$^{II}$ ions in a square-planar environment (with an intra-chain Cu—Cu distance of 8.226 Å). Each Cu$^{II}$ ion is coordinated by two oxygen and two nitrogen atoms. The individual chains are well separated and interact only through weak van der Waals bonds. Note that the distance between the Cu$^{II}$ ions of adjacent chains is 5.169 Å along the *a*-direction and 7.961 Å along the *b*-axis [4].

According to the $\chi_{mol}$ (T) data below 1 K, *CuCCP* lacks a phase transition into a long-range ordered magnetic state above 0.06 K which highlights its 1-D character [5]. Selected bond length and bond angles for *TK 91*, *TK 251*, *TK 102* and *CuCCP* are listed in Table 1 together with key parameters characterizing the magnetic properties of these compounds.

## 3. Magnetic susceptibility

The magnetic characterization of all samples was carried out by employing a Quantum-Design SQUID magnetometer in the temperature range from 300 K to 2 K and fields up to 5 T. In the temperature range 0.06 K ≤ T ≤ 2.0 K, the magnetic susceptibility was

Table 1
Selected bond length, bond angles and magnetic parameter for the dimer compounds *TK 91*, *TK 251* and *TK 102* and the antiferromagnetic Heisenberg spin chain *CuCCP*

|  | *TK 102* | *TK 251* | *TK 91* | *CuCCP* |
|---|---|---|---|---|
| Bond lengths (Å) |  |  |  |  |
| Cu—O(1) | 1.880(2) | 1.921(3) | 1.9297(12) | 1.8(1) |
| Cu—N(1) | 1.917(3) | 1.969(5) | 1.9653(16) | 2.0(1) |
| Cu—O(2) | 1.965(2) | 2.012(4) | 2.0010(14) | 1.8(1) |
| Cu—N(2) | 2.076(3) | 2.089(4) | 2.0754(15) | 2.0(1) |
| Cu—O(1)#1 |  | 2.514(4) | 2.4344(13) |  |
| Cu—O(3) |  | 2.534(5) | 2.5652(16) |  |
| Angles (deg) |  |  |  |  |
| O(1)—Cu—N(1) | 94.03(11) | 92.78(16) | 90.85(6) | 97(1) |
| O(1)—Cu—O(2) | 89.77(10) | 87.64(15) | 88.07(5) | 83(1) |
| N(1)—Cu—N(2) |  |  |  | 180(2) |
| O(1)—Cu—O(2) |  |  |  | 180(2) |
| N(1)—Cu—O(2) | 170.78(13) | 173.24(19) | 175.04(6) |  |
| O(1)—Cu—N(2) | 169.88(12) | 172.93(18) | 175.61(6) |  |
| N(1)—Cu—N(2) | 86.20(11) | 92.95(18) | 93.51(6) |  |
| O(2)—Cu—N(2) | 91.55(10) | 87.16(16) | 87.55(6) |  |
| Magnetic parameter |  |  |  |  |
| $g_z$ | 2.22 |  | 2.27 | 2.14 |
| $g_{x,y}$ | 2.06 |  | 2.04 | 2.01 |
| afm $\Theta_{CW}$ | 2.2 K | 3.7 K | 6.6 K | 25.0 K |
| $\mu_{eff}$ (300 K) | 1.95$\mu_B$ | 1.83$\mu_B$ | 1.91$\mu_B$ | 1.96$\mu_B$ |
| $J_1/k_B$ | 4.0 K | 7.8 K | 9.9 K | 21.5 K |
| $\alpha$ | 0.00 | 0.05 | 0.10 | 1.00 |

determined with an ac-technique in a top loading $^3$He/$^4$He dilution refrigerator.

In the temperature range from 300 K to 50 K, the molar magnetic susceptibilities of the dimer compounds *TK 102*, *TK 91* and *TK 251* exhibit a Curie–Weiss-like behavior with antiferromagnetic Curie–Weiss temperatures of $\Theta_{CW} = 6.6$ K (*TK 91*), 3.7 K (*TK 251*) and 2.2 K (*TK 102*). The effective magnetic moments at room temperature for all dimer compounds range from 1.81$\mu_B$ to 1.95$\mu_B$. They are slightly enhanced in comparison to the value of a free Cu$^{II}$ ion (1.73$\mu_B$) and exhibit only a weak temperature dependence down to 25 K. These magnetic parameters are a clear indication that the magnetic coupling constants in these novel dimer compounds are of only moderate strength as expected for the modified hydroquinone linkers employed.

Fig. 3 exhibits $\chi_{mol}$ (T) for a single crystal of the coupled-dimer compounds *TK 91* (open squares) and pressed powder samples of *TK 251* (filled triangles) together with the pressed powder sample of the isolated-dimer system *TK 102* (open circles). After subtracting the diamagnetic core contribution for the different materials, the data have been fitted by employing a numerical expression given in Ref. [6]. This function has been used to describe especially the
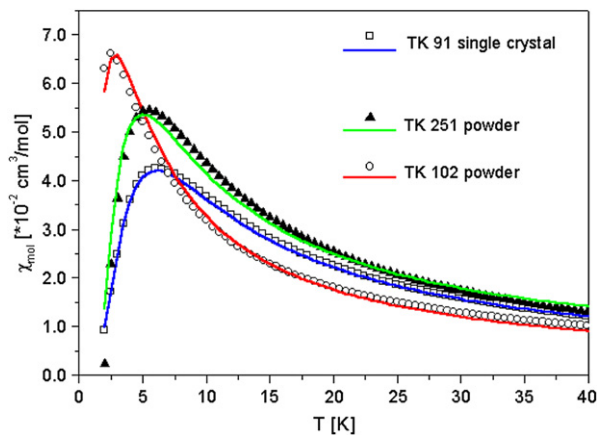
Fig. 3. Magnetic susceptibility as a function of temperature for the different dimer compounds. Open squares *TK 91*, filled triangles *TK 251* and open circles *TK 102*. The solid lines are fits to the experimental data according to Ref. [5]. The Curie-contribution of uncoupled $S = 1/2$ spins was included in the fitting procedure. The following amount of uncoupled $S = 1/2$ spins has been subtracted: *TK 91* (single crystal) 0.5%; *TK 102*; *TK 251* (powder) 40%.
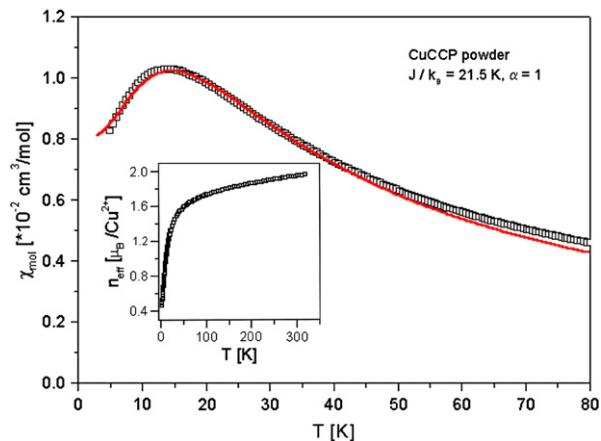


Fig. 4. Magnetic susceptibility as a function of temperature of the uniform $S = 1/2$ antiferromagnetic Heisenberg spin chain *CuCCP*. The solid line is a fit to the experimental data according to Ref. [5]. The inset shows the effective magnetic moment of *CuCCP* for temperatures $2 \text{ K} \leq T \leq 320 \text{ K}$. A Curie-contribution of 4% uncoupled $S = 1/2$ spins has been subtracted from the data.

low-temperature susceptibility of spin chains with dimerisation parameters $\alpha = J_2/J_1$ ranging from $\alpha = 0$ (isolated dimer) to 1 (uniform Heisenberg spin chain), employing the dominant magnetic coupling constant $J_1$ and $\alpha$ as fit parameters. The Curie-contribution of uncoupled $S = 1/2$ spins was included in the fitting procedure and had been subtracted from the data displayed in Fig. 3. The content of uncoupled spins in the dimer compounds varies between 0.5% for high-quality single crystals of *TK 91* and approximately 40% for both powder samples *TK 251* and *TK 102*.

The solid lines in Fig. 3 are fits to the experimental data, employing the expression given in Ref. [6]. The so-derived antiferromagnetic coupling constants $J_1$ and dimerisation parameters $\alpha$ are listed in Table 1. The data clearly indicate that $J_1$ and $\alpha$ become reduced on going from *TK 91* over *TK 251* to *TK 102*.

Fig. 4 shows the molar magnetic susceptibility $\chi_{mol}$ of a pressed powder sample of *CuCCP* as a function of temperature for $T \leq 80 \text{ K}$, see also Ref. [2]. The data have been corrected for the paramagnetic signal of uncoupled $S = 1/2$ spins and the temperature-independent diamagnetic core contributions. Fitting the low-temperature data for $0.06 \text{ K} \leq T \leq 1.1 \text{ K}$ to a Curie−Weiss-law, we obtained a concentration of 4% uncoupled $S = 1/2$ spins with a very small antiferromagnetic Curie−Weiss temperature of $\Theta_{CW} \sim -10 \text{ mK}$ [2,5].

For high temperatures and down to 120 K, $\chi_{mol}$ (T) of *CuCCP* follows a Curie−Weiss-like temperature dependence with an antiferromagnetic Curie−Weiss temperature $\Theta_{CW} \sim 25 \text{ K}$. Upon cooling, $\chi_{mol}$ (T) exhibits a broad maximum around 15 K, typical for a 1-D antiferromagnet [6]. For temperatures below 15 K, $\chi_{mol}$ (T) slowly decreases, extrapolating to a finite value for $T \to 0$ as expected for a 1-D uniform afm $S = 1/2$ Heisenberg spin chain [6,7]. The solid line in Fig. 4 is a fit to the experimental data employing the expression given in Ref. [6] from which an antiferromagnetic intra-chain coupling constant $J = 21.5 \text{ K}/k_B$ has been obtained [2]. The absence of a 3-D magnetic ordering down to 0.06 K implies a ratio of inter-chain to intra-chain coupling $J_\perp/J < 10^{-4}$ [8]. According to these distinct magnetic properties, the coordination polymer *CuCCP* can be considered an excellent model system for a 1-D $S = 1/2$ antiferromagnetic Heisenberg chain.

The inset of Fig. 4 displays the temperature dependence of the effective magnetic moment of the Cu[II] ions in *CuCCP*. In the temperature range from 300 K down to 100 K, the effective magnetic moment becomes slightly reduced from $1.95\mu_B$ to $1.76\mu_B$. Below 100 K, the magnetic coupling between the individual Cu[II] ions, which causes the formation of 1-D antiferromagnetic Heisenberg spin chain, leads to the strong reduction of $\mu_{eff}$ below 100 K clearly seen in the inset of Fig. 4.

## 4. Ab initio calculations

We have investigated the electronic properties of the Cu-based organometallic systems by performing

ab initio density functional calculations within the generalized gradient approximation (GGA) [9]. As a basis set, we considered the linearized muffin tin orbital method (LMTO) based on the Stuttgart TBLMTO-47 code [10]. Our aim has been to get a reliable estimate of the nature of the interaction paths in these compounds based on the ab initio calculations. For this purpose, we applied the tight-binding-downfolding procedure [11] which obtains the effective $Cu_d$–$Cu_d$ hopping parameters by downfolding all the degrees of freedom in the band structure calculation other than the $Cu_d$ bands at the Fermi level. We analyzed two systems, the polymer *CuCCP* and the coupled-dimer system *TK 91*.

The predominant hopping path, $t = 79$ meV, obtained from the *CuCCP* system, is between Cu neighbors along the chain. This path is mediated by the hydroquinone linker. The next important hopping term is almost an order of magnitude smaller than $t$, $t' = 8$ meV and defines the effective interaction path between coppers belonging to different chains along the *a*-direction. This ab initio calculation confirms the experimental observation that *CuCCP* is a quasi-one dimensional system with weak inter-chain interactions.

A rough estimate of the antiferromagnetic superexchange between the Cu ions along the chain can be obtained by using the expression $J = 4t^2/U_{eff}$, where $U_{eff}$ is the effective onsite Coulomb repulsion on the Cu site and $t$ is the ab initio derived hopping integral. Considering usual $U_{eff}$ values for Cu oxides $U_{eff} = 4$–$6$ eV we get an estimate $J \sim 58$ K ($U_{eff} = 5$ eV) which is somewhat above the experimental value but remains of the same order of magnitude. A detailed ab initio investigation of this system including structural relaxation studies and chemically modified *CuCCP* structures has been presented in Ref. [12].

The coupled-dimer system *TK 91* was also investigated with the downfolding method. Interestingly, we found that the strongest interaction path $t = 43$ meV is between coppers that are as far apart as 8.4 Å and linked by the hydroquinone group, while the hopping between nearest neighbor coppers at a distance of 3.4 Å is almost zero. The next relevant hopping term $t'$ is between fifth nearest neighbor Cu ions along the *a*-direction $t' = 23$ meV. The description of *TK 91* concluded from these calculations is that of Cu dimers containing the hydroquinone as bridging ligand. These dimers are weakly coupled within the 3-dimensional structure. An estimate of the intradimer coupling can be obtained − as in the case of *CuCCP* − by considering the expression $J = 4t^2/U_{eff}$ with $t$ being the intradimer

hopping integral. We obtain $J \sim 17$ K which, though overestimating the experimental value somewhat, is within the same order of magnitude.

## 5. Electron-spin resonance

The magnetic resonance experiments were performed in the mm- and sub-mm-wave region between 28 and 420 GHz using Gunn- and IMPATT-diode together with frequency multipliers in a home-built spectrometer. For measurements with frequencies up to 42 GHz, specially designed cavities were used.

Electron-spin resonance (ESR) experiments on single crystals of *TK 91* were carried out in the frequency range 26–40 GHz and for temperatures $4.2$ K $\leq T \leq 140$ K. The ESR measurements detect two non-equivalent magnetic centers of copper ions at any orientation of the sample with respect to the applied magnetic field. Each of these has an axial anisotropy with the *g*-values in the range of 2.04–2.27 at $T = 108$ K. The local magnetic axes of these centers are almost perpendicular to each other. The axial anisotropy is in accordance with the local environment of this coupled-dimer compound determined by X-ray crystal structure analysis.

Fig. 5 exhibits a typical ESR single-crystal spectrum of *TK 91* at $T = 108$ K and a frequency of 39.852 GHz. The narrow line is the signal of a small amount of the free stable radical DPPH used for calibration. The two non-equivalent $Cu^{II}$ centers are clearly visible in the excitation spectrum. The inset of Fig. 5 displays a picture of a single crystal of *TK 91*. Also indicated in the
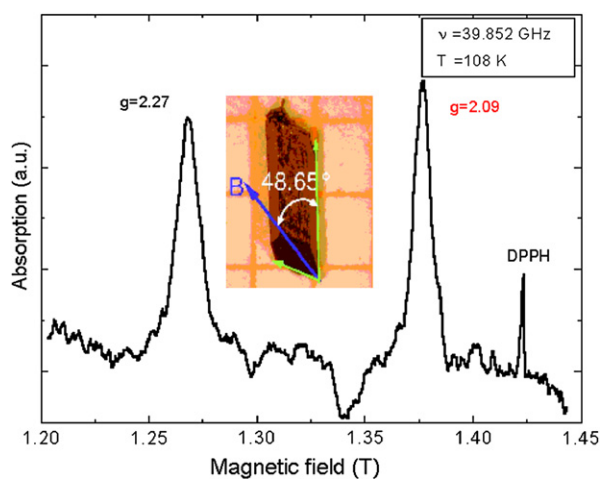
Fig. 5. ESR resonance for a single crystal of *TK 91* at 108 K. The inset displays a picture of the single crystal together with the orientation of the principal magnetic axes of a $Cu^{II}$ center. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

inset is the orientation of the applied magnetic field (blue arrow) which is tilted by 48.65° with respect to the *a*-axis of the single crystal. In this orientation, the external field is parallel to one of the principal magnetic axes of a $Cu^{II}$ center with $g = 2.27$. In this field orientation, the second $Cu^{II}$ center exhibits a $g$-value of 2.09. The values of these $g$-factors are directly connected with the local environment of the $Cu^{II}$ ions and they are in the range which is expected for sixfold coordinated copper ions [13].

Fig. 6 shows the typical ESR signal of a powder sample of the isolated-dimer compound *TK 102*. The data were taken at 2.75 K, i.e., around the maximum of the magnetic susceptibility. The special shape of this broad resonance is due to the averaging of over all possible field orientations of the copper centers in the powdered sample. From the edges of the powder-resonance spectrum, we determined the extremal $g$-factors $g_z = 2.22$ and $g_{x,y} = 2.06$, which have a temperature variation of only 0.1% between 120 K and 2 K. These $g$-factors differ clearly from the values determined for *TK 91*. The difference is approximately 2.2% for $g_z$ and 1.4% for $g_{x,y}$ directly reflecting changes in the coordination and local environment of the $Cu^{II}$ ions, on passing from an elongated octahedral (*TK 91*) structure to a distorted square-planar (*TK 102*) environment.

Fig. 7 shows the powder spectra for *CuCCP* taken at the high frequency of 330 GHz and temperatures of 29.7 K and 5.7 K. The temperature dependence of the integrated signal is in accordance with $\chi_{mol}$ (T). It is obvious that in this temperature range $g_z$ and $g_{x,y}$ are temperature independent with values of $g_z = 2.14$ and $g_{x,y} = 2.01$. These numbers are comparable with $g$-values expected for a $Cu^{II}$ ion in a square-planar coordination [13]. A comparison with the $g$-factors of *TK 102*
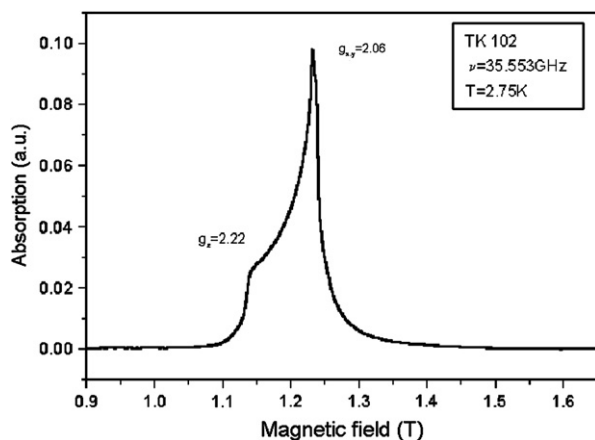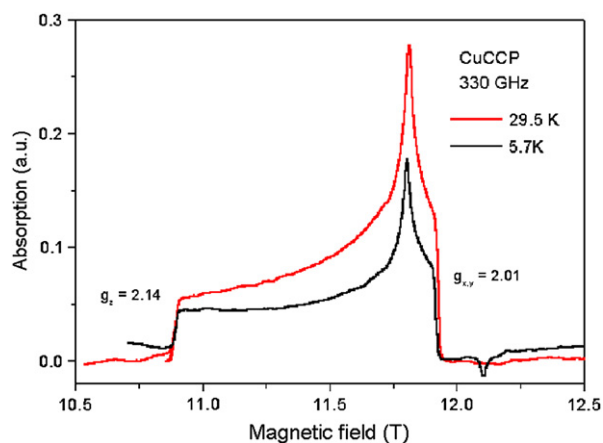


Fig. 7. ESR resonance of a powder sample of the 1-D Heisenberg spin chain *CuCCP* at 5.7 K and 29.7 K determined at a frequency of 330 GHz.

reveals a difference of approximately 3.7% for $g_z$ and 2.5% for $g_{x,y}$. Again, this behavior indicates the strong influence of the local Cu environment. A deviation from the square-planar $Cu^{II}$ coordination to a distorted one leads to these large differences in the $g$-factors.

## 6. Discussion

The anisotropies of the $g$-values found in the ESR experiments for the present series of hydroquinone-based low-dimensional $Cu^{II}$ quantum-spin systems are in agreement with the structural investigations on the various compounds. The question at hand is whether there is a correlation between the structural and magnetic properties within this series of compounds. In all systems described in this paper, the dominant magnetic exchange is mediated by the modified hydroquinone linkers. As expected, the magnetic exchange is of moderate size for all systems ranging from $J/k_B = 21.5$ K (*CuCCP*) to $J_1/k_B = 4.0$ K for *TK 102*. Table 1 indicates that a correlation exists between the size of $J/k_B$ and the extent to which the $Cu^{II}$ ion is dislocated from the O(1,2)N(1,2)-plane. *CuCCP*, possessing the largest coupling constant of $J/k_B = 21.5$ K within this new series of low-dimensional spin systems, has its $Cu^{II}$ centers in an ideal square-planar coordination environment. Each $Cu^{II}$ ion lies precisely within the O(1,2)N(1,2)-plane and the angles N(1)−Cu−O(2) and O(1)−Cu−N(2) are 180° resulting in a magnetic coupling constant of $J/k_B = 21.5$ K. If the position of the $Cu^{II}$ ion is slightly above the $O_2N_2$-plane as in *TK 91*, where the angles N(1)−Cu−O(2) and O(1)−Cu−N(2) are 175.04° and 175.61°, respectively, the coupling constant $J_1/k_B$ is reduced to 9.9 K. This trend continues



Fig. 6. ESR resonance of a powder sample of *TK 102* at 2.75 K and 35.55 GHz.

for *TK 102* exhibiting a coupling constant of 4.0 K and bond angles for $Cu^{II}$ of 170.78° and 169.88°. Calculating the displacements $u$ of the $Cu^{II}$ ions from the distortion angles we obtained a nearly linear dependence between $J/k_B$ and $u$ with a value of $-(109 \pm 9)$ K/Å.

## 7. Summary

We have synthesized a new family of low-dimensional quantum-spin systems based on hydroquinone-derived linkers connecting $Cu^{II}$ ions carrying a spin of $S = 1/2$. This family includes isolated $Cu^{II}$ dimers, various coupled $Cu^{II}$-dimer systems and a 1-D uniform $S = 1/2$ Heisenberg antiferromagnetic chain. The antiferromagnetic coupling constants are of moderate strength with values in the range from $J/k_B = 21.5$ K to 4.0 K. By relating the magnetic properties to the structural features of the individual compounds of this family, we have been able to deduce a correlation between the size of the magnetic coupling constant and the position of the $Cu^{II}$ ions. An increase of the displacement of the Cu ion with respect to the ideal square-planar coordination leads to a near linear decrease of $J$ within this series of compound, where the magnetic coupling is mediated by modified hydroquinone linkers.

In addition, the first principles calculations performed here are valuable hints for understanding the nature of the microscopic interactions in these organometallic systems.

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