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# Cobalt(II)–Copper(II) Bimetallic Chains as a New Class of Single-Chain Magnets**

By *Emilio Pardo, Rafael Ruiz-García, Francesc Lloret,* *Juan Faus, Miguel Julve, Yves Journaux, Fernando Delgado,* and *Catalina Ruiz-Pérez*

Magnetic chain compounds have been actively investigated in the field of molecular magnetism for the design and synthesis of molecule-based magnets because of their possibility to achieve long-range magnetic order via interchain interactions.[1,2] Recent findings regarding magnetic hysteresis effects on one-dimensional (1D) compounds,[3] which are not associated with a three-dimensional (3D) magnetic order but with a slow magnetic relaxation, have provided an experimental confirmation of Glauberts' prediction[4] and opened exciting new perspectives of storing information in low-dimensional magnetic materials.

The reported examples of these so-called molecular magnetic nanowires or single-chain magnets (SCMs) are: i) [Co-(hfacac)$_2$(NITPhOMe)] (hfacac = hexafluoroacetylacetonate, NITPhOMe = 4′-methoxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) which is a ferrimagnetic chain composed of high-spin cobalt(II) ions and nitronyl nitroxide radicals alternately arranged in a trigonal helix;[3] ii) [Mn$_2$(saltmen)$_2$-Ni(pao)$_2$L$_2$](A)$_2$ [saltmen = N,N′-1,1,2,2-tetramethylethylenebis(salicylideneiminate), pao = pyridine-2-aldoxime, L = pyridine (py), 4-picoline (4-pic), 4-*tert*-butylpyridine (4-*t*Bupy),

N-methylimidazole (N-Meim), A = ClO$_4^-$, BF$_4^-$, PF$_6^-$, ReO$_4^-$] which consist of chains of Mn$^{III}$Ni$^{II}$Mn$^{III}$ trinuclear units with alternating intratrimer antiferro- and intertrimer ferromagnetic interactions through oximato and phenolato bridges, respectively;[5] iii) [[FeL-(CN)$_4$]$_2$Co(H$_2$O)$_x$] [L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen)] which are single (x = 2) or double (x = 1) zigzag cyanide-bridged chains with ferromagnetic coupling between the low-spin iron(III) and high-spin cobalt(II) ions,[6] and iv) [Co(bt)(N$_3$)$_2$] (bt = 2,2′-bithiazoline) which is a ferromagnetic chain made up of azide-bridged high-spin cobalt(II) ions in an helical arrangement.[7]

Here we report the X-ray structure[8] and magnetic properties[9] of a new example of a single-chain magnet of formula [CoCu(2,4,6-tmpa)$_2$(H$_2$O)$_2$]·4H$_2$O (**1**; see Fig. 1) (2,4,6-tmpa = N-2,4,6-trimethylphenyloxamate), which is obtained by reaction of the anionic oxamatocopper(II) complex [Cu(2,4,6-tmpa)]$^{2-}$ (see below) with cobalt(II) cations.
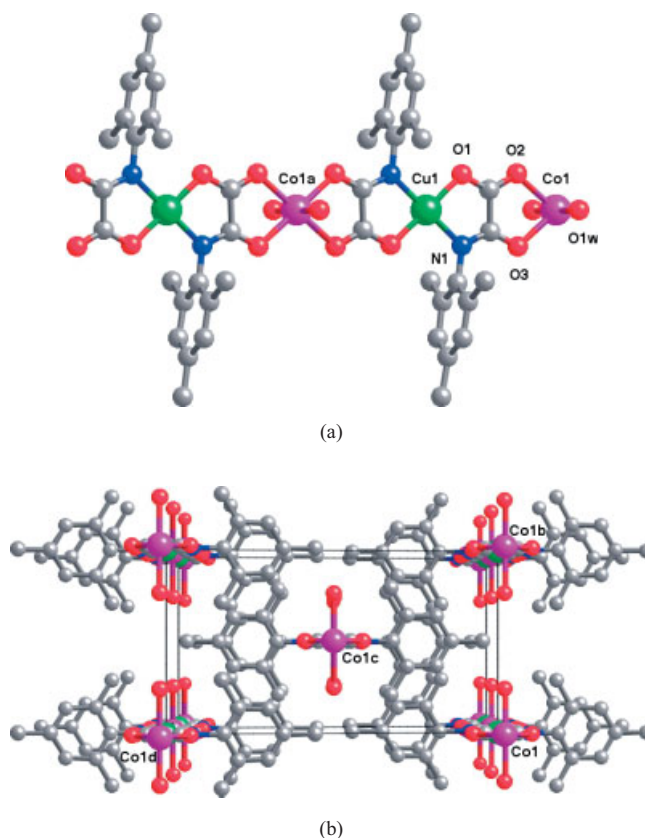


(a)



(b)

**Figure 1.** a) View of a fragment of the bimetallic chain of **1** (atom types are indicated, labeling of hydrogen atoms and carbon atoms was omitted for the sake of clarity). b) Perspective drawing of the crystal packing of **1** along the *c* axis. Selected intermetallic distances (Å) with standard deviations in parentheses: Co1–Cu1 5.3010(15), Co1–Co1a 10.602(3), Co1–Co1b 8.702(3), Co1–Co1c 9.076(3), Co1–Co1d 15.930(3) [symmetry codes: a) = x, y, z + 1; b) = x, y + 1, z; c) = x − 1/2, y − 1/2, z; d) = x + 1, y, z].
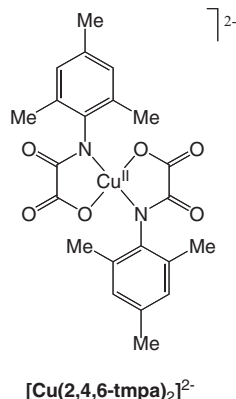
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**[Cu(2,4,6-tmpa)$_2$]$^{2-}$**

Complex **1** consists of neutral ribbon-like oxamato-bridged Co$^{II}$Cu$^{II}$ chains and crystallization water molecules. Within each chain, the bis(oxamato)copper(II) entity acts as a bis-bidentate ligand through the *cis* carbonyl oxygen atoms towards *trans* diaquacobalt(II) units, affording bimetallic chains which run parallel to the *c* axis (Fig. 1a). The copper atom is four coordinate with two amide nitrogen atoms and two carboxylate oxygen atoms from the two oxamate ligands in a *trans* arrangement building a square-planar surrounding [1.949(3) and 1.958(3) Å for Cu1–N1 and Cu1–O1, respectively]. The cobalt atom is six coordinate with two *trans* coordinated water molecules and four oxygen atoms from two oxamate ligands forming a distorted octahedral surrounding. The bond lengths around the cobalt atom [2.158(5), 2.109(3), and 2.066(3) Å for Co1–O1w, Co1–O2, and Co1–O3, respectively] are similar to those observed for the high-spin cobalt(II) ion in the oxamidato- and carboxylato-bridged bimetallic chain compound [Cu(obp)Co(H$_2$O)$_3$]·H$_2$O (H$_4$obp = oxamide-*N,N'*-dipropionic acid).[10] The phenyl ring which is practically perpendicular to the oxamate group [the value of the dihedral angle between their mean planes is 89.75(22)°] affords an effective shielding between neighboring chains in the *ab* plane (Fig. 1b). Weak interchain hydrogen bonding interactions exist along the *b* axis via the coordinated water molecules and the crystallization ones [2.878(6) Å for O1w···O2w] which define a square motif (Fig. S1, Supporting Information).

The magnetic behavior of **1** under the form of $\chi_M T$ versus $T$ plot, $\chi_M$ being the direct current (DC) magnetic susceptibility per CoCu pair, is characteristic of a 1D ferrimagnetic chain compound (Fig. 2a).[11] At room temperature, $\chi_M T$ is equal to 2.60 cm$^3$ mol$^{-1}$ K, a value which is significantly below that expected for a square-planar copper(II) ion ($S_{Cu}$ = ½) and a octahedral high-spin cobalt(II) ion ($S_{Co}$ = 3⁄2) with an orbitally degenerate $^4$T$_1$ single-ion ground state ($L_{Co}$ = 1), considered as magnetically isolated. This fact suggests the occurrence of a relatively large intrachain antiferromagnetic interaction between the Cu$^{II}$ and Co$^{II}$ ions which is confirmed by the shape of the $\chi_M T$ versus $T$ plot. Upon cooling, $\chi_M T$ decreases first, it attains a minimum at 90 K, with $\chi_M T$ = 2.18 cm$^3$ mol$^{-1}$ K (inset: Fig. 2a), and then increases to reach a maximum at 7.0 K, with $\chi_M T$ = 41.0 cm$^3$ mol$^{-1}$ K, owing to saturation effects. The lack of a DC susceptibility maximum together with the ab-
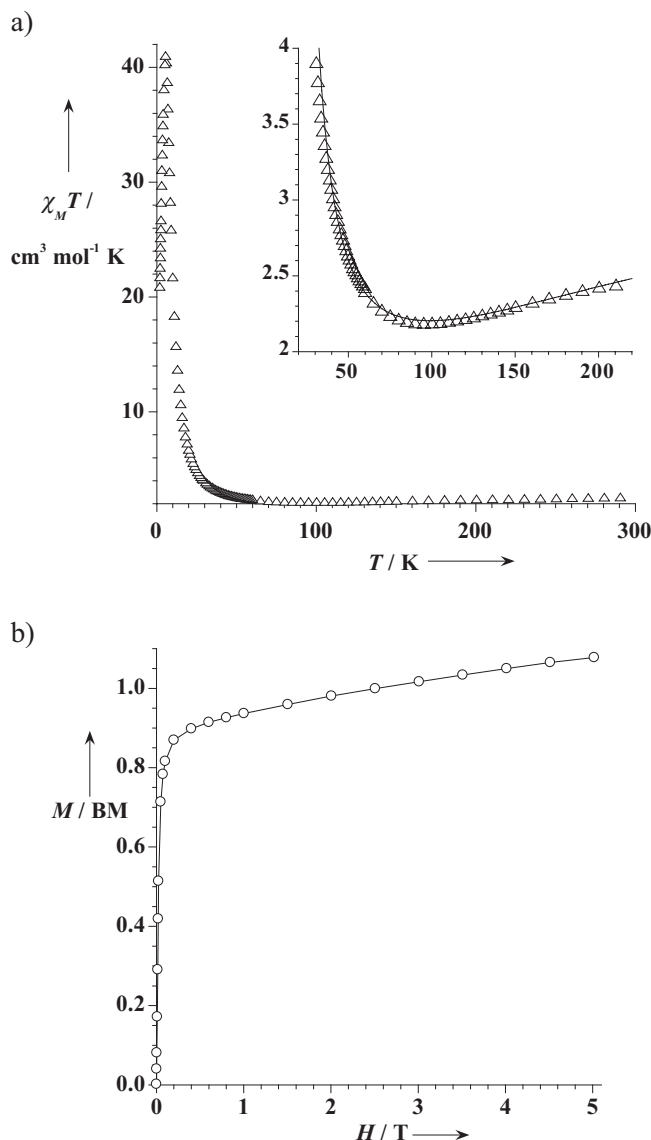
a)

b)

**Figure 2.** a) Temperature dependence of $\chi_M T$ of **1** under an applied magnetic field of 1 T ($T \geq 50$ K) and 250 Oe ($T < 50$ K). The inset shows the minimum of $\chi_M T$. The solid line is the best-fit curve [11]. b) Field dependence of $M$ of **1** at 2.0 K. The solid line is an eye-guide.

sence of a λ-peak in the heat capacity measurements on polycrystalline samples of **1** (not shown) allows us to rule out the occurrence of a 3D long-range magnetic order, thus showing that the chains are magnetically well isolated. The $M$ versus $H$ plot for **1** at 2.0 K, $M$ being the magnetization per CoCu pair and $H$ the applied magnetic field, shows a fast saturation with ca. 80 % of the maximum magnetization value reached within a field of 2000 Oe (1 Oe = 1000/4π A m$^{-1}$; Fig. 2b). This reveals a strong short-range correlation along the chain favoring the antiparallel alignment of the spins of Cu$^{II}$ and Co$^{II}$ ions.

Interestingly, **1** exhibits in-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) alternating current (AC) magnetic susceptibility signals at low temperatures which are frequency-dependent (Fig. 3).
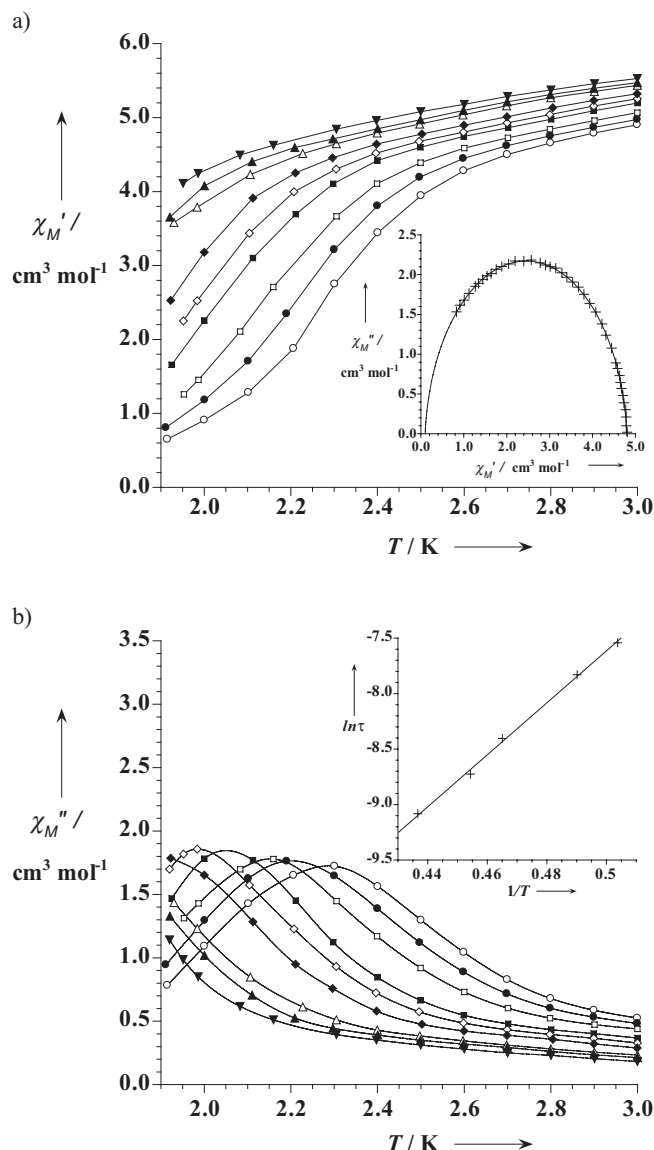
**Figure 3.** Temperature dependence of a) $\chi_M'$ and b) $\chi_M''$ of **1** in zero applied static field and under 1 Oe oscillating field at different frequencies of the oscillating field: (▼) 50, (▲) 75, (△) 100, (◆) 200, (◇) 300, (■) 400, (□) 700, (●) 1000, (○) 1400 Hz. The solid lines are eye-guides. The insets show a) the Cole–Cole plot at 2.0 K and b) the Arrhenius plot (see text).

$\chi_M'$ begins to decrease and $\chi_M''$ becomes different from zero between 5.0 K (1400 Hz) and 3.0 K (50 Hz). In addition, $\chi_M''$ shows maxima between 2.3 K (1400 Hz) and 2.0 K (300 Hz). This behavior is indicative of slow magnetic relaxation effects which are typical of SCMs.[3,5–7] Indeed, the $\chi_M''$ versus $\chi_M'$ plot at 2.0 K (Cole–Cole plot) in the frequency range 1.0–1400 Hz gives an almost perfect semicircle (inset of Fig. 3a), supporting only one relaxation process and discarding spin-glass behavior for **1**. This is confirmed by the small value of the $\alpha$ parameter of 0.05 obtained by the least-squares fit of the experimental data through a generalized Debye model with adiabatic ($\chi_S$) and isothermal ($\chi_T$) susceptibility values of

0.1 and 4.7 cm³ mol⁻¹, respectively ($\alpha = 0$ for an ideal Debye model with a single relaxation time).[12] The relaxation time ($\tau$) for **1** follows the Arrhenius law [$\tau = \tau_0 \exp(E_a/k_B T)$] characteristic of a thermally activated mechanism, with an energy barrier ($E_a$) to reverse the magnetization direction of 16.3 cm⁻¹ and a pre-exponential factor ($\tau_0$) of $4.0 \times 10^{-9}$ s (inset of Fig. 3b). However, these values must be regarded with caution because of the very narrow temperature range available.

To conclude, complex **1** is the first example of an oxamato-bridged heterobimetallic chain compound which behaves as a SCM and its existence expands the range of the few reported examples of slow magnetic relaxing 1D materials. The combination of an orbitally degenerate high-spin cobalt(II) ion and a copper(II) complex with sterically hindered aromatic group-substituted oxamate ligands cause a large Ising-type magnetic anisotropy and minimize interchain interactions, respectively, in **1**. It is envisioned that this approach will lead to the development of a new family of SCMs via ligand design by playing with the steric requirements of the substituents in the copper(II) precursor.

## Experimental

*H₂-2,4,6-tmpa*: The proligand was isolated as the ethyl ester derivative by reacting 2,4,6-trimethylaniline (8.6 mL, 60.0 mmol) and ethyl oxalyl chloride (7.0 mL, 60.0 mmol) in tetrahydrofuran (THF) (150 mL) at 0 °C and under continuous stirring. The resulting transparent yellow solution was refluxed for 1 h and the solvent was removed in a rotatory evaporator leaving an orange oil. This oil solidified when left at room temperature. The white solid was collected and washed with dried diethyl ether (90 %). Elemental analysis calcd (%) for $C_{13}H_{17}NO_3$ (235.1): C 66,40, H 7.23, N 5.95; found: C 66.31, H 6,99, N 5.86; ¹H NMR ([D₆]DMSO): $\delta = 1.05$ (t, 3H; CH₃), 1.90 (s, 3H; CH₃), 2.05 (s, 6H; 2CH₃), 4.05 (q, 2H; CH₂O), 6.70 (s, 2H; 3H and 5H of $C_6H_2N(CH_3)_3$), 9.95 (s, 1H; NH); IR (KBr): $\nu = 3390$ (N–H), 3050, 2975, 2870 (C–H), 1680, 1645, 1630 cm⁻¹ (C=O).

*Na₂[Cu(2,4,6-tmpa)₂]·6H₂O*: The anionic copper(II) precursor was isolated as the hexahydrate sodium salt by reaction of the ethyl ester derivative of H₂-2,4,6-tmppa (2.35 g, 10.0 mmol), NaOH (1.0 g, 25.0 mmol), and Cu(NO₃)₂·3H₂O (1.21 g, 5.0 mmol) in water (75 mL) at room temperature under stirring. The resulting deep green solution was then filtered on paper in order to eliminate the remainder of the solid particles. The solvent was reduced to a half volume in a rotatory evaporator, after a precipitate began to appear. The green polycrystalline solid was then collected via filtration, washed with acetone and diethyl ether, and dried under vacuum (75 %). Elemental analysis calcd (%) for $C_{22}H_{34}CuN_2Na_2O_{12}$ (627.8): C 42.09, H 5.42, N 4.46; found: C 41.95, H 5.25, N 4.39; IR (KBr): $\nu = 3440$, 3290, 3190 (O–H), 3020, 2980, 2950, 2910, 2860 (C–H), 1685 and 1650 cm⁻¹ (C=O).

*Complex 1*: Well-formed deep green octahedral prisms of **1** were obtained via slow diffusion in an H-shaped tube of aqueous solutions containing stoichiometric amounts of Na₂[Cu(2,4,6-tmpa)₂]·6H₂O (0.150 g, 0.25 mmol) in one arm and Co(NO₃)₂·6H₂O (0.073 g, 0.25 mmol) in the other one. They were collected on filter paper and air-dried. Elemental analysis calcd (%) for $C_{22}H_{34}CuN_2CoO_{12}$ (640.7): C 41.24, H 5.31, N 4.37; found: C 41.05, H 5.23, N 4.25; IR (KBr): $\nu = 3405$ (O–H), 3015, 2970, 2945, 2910, 2850 (C–H), 1590 cm⁻¹ (C=O).

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[8] Crystal data for **1**: $C_{22}H_{34}CoCuN_2O_{12}$, $M_r = 640.98$, monoclinic, space group $C2/m$, $a = 15.930(3)$, $b = 8.702(3)$, $c = 10.602(3)$ Å, $\beta = 99.54(2)°$, $V = 1449.4(7)$ Å$^3$, $T = 293$ K, $Z = 2$, $\rho_{calcd} = 1.453$ g cm$^{-3}$, $\mu$(Mo Kα) = 1.365 mm$^{-1}$. 2212 unique reflections, and 1446 observed with $I > 2\sigma(I)$. All the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with full-matrix least-squares technique on $F^2$ using the SHELXS-97 and SHELXL-97 programs. The hydrogen atoms from the organic ligand were calculated and refined with isotropic thermal parameters, while those from the water molecules were neither found nor calculated. Refinement of 110 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0531$ and $R_w = 0.1107$, with $S = 1.004$. The final Fourier-difference map showed maximum and minimum height peaks of 0.51 and –0.34 e Å$^{-3}$. 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-227 520. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223–336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] Variable-temperature (1.8–300 K) DC and AC magnetic susceptibility measurements and variable-field (0–5 T) DC magnetization measurements were carried out on a polycrystalline sample of **1** with a Quantum Design SQUID magnetometer. The magnetic data were corrected for the diamagnetism of the constituent atoms and the sample holder.

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[11] We have performed a preliminary analysis of the magnetic data of **1** through the branch chain model previously developed for the related oxamato-bridged bimetallic chain compound [CoCu(pbaOH)(H$_2$O)$_3$]· 2H$_2$O [pbaOH = $N$,$N'$-2-hydroxy-1,3-propylenebis(oxamato)]; P. J. Van Kroningsbruggen, O. Kahn, K. Nakatani, Y. Pei, J. P. Renard, M. Drillon, P. Legoll, *Inorg. Chem.* **1990**, *29*, 3325. In this model, it is assumed that only $z$ components of spin and orbital momenta are coupled and that the applied magnetic field is along the quantization axis. The corresponding Hamiltonian is then written as $H = \sum_i [-J[S_{Co,i(z)}(S_{Cu,i(z)} + S_{Cu,i-1(z)})] + J' \cdot L_{Co,i(z)} \cdot S_{Co,i(z)} + D \cdot L_{Co,i(z)}^2 - \beta \cdot H_{(z)}(g_{Co} \cdot S_{Co,i(z)} + g_{Cu} \cdot S_{Cu,i(z)} + k \cdot L_{Co,i(z)})]$, where $i$ runs over CoCu units, $L_{Co}$ is the orbital momentum, $J$ and $J'$ are the exchange and spin-orbit coupling parameters, $\kappa$ and $D$ are the orbital reduction and local anisotropy parameters of the cobalt(II) ion, and $g_{Co}$ and $g_{Cu}$ are the Landée factors. Least-squares fit of the $\chi_M T$ data

of **1** through this model in the temperature range 30–290 K reproduces well the observed minimum (solid line in the inset of Fig. 2a), with $J = -26.6$ cm$^{-1}$, $J' = 91.5$ cm$^{-1}$, $\kappa = 0.8$, $D = -188.0$ cm$^{-1}$, $g_{Co} = 2.38$, and $g_{Cu} = 2.05$. The antiferromagnetic exchange coupling between copper(II) and cobalt(II) ions in **1** is somewhat stronger than that reported for [CoCu(pbaOH)(H$_2$O)$_3$]·2H$_2$O ($J = -18.0$ cm$^{-1}$). The fact that the copper atom in **1** lies in the oxamato plane (CuN$_2$O$_2$ chromophore in a square-planar surrounding), whereas it is out of this mean plane in the related pbaOH compound (CuN$_2$O$_3$ chromophore in a square-pyramidal environment), leads to a better overlap of the magnetic orbitals through the σ in-plane exchange pathway, and thus to a larger antiferromagnetic coupling in **1**. The effective spin-orbit coupling can be related with the spin-orbit coupling parameter $\lambda$ through the expression $J' = -A\kappa\lambda$. This gives $\lambda = -110$ cm$^{-1}$ (with $A = 3/2$) for the cobalt(II) ion in **1** (compared with $\lambda_0 = -180$ cm$^{-1}$ for the free ion).

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# Patterned Alignment of Liquid Crystals by μ-Rubbing**

By *Soney Varghese, Sunil Narayanankutty, Cees W. M. Bastiaansen,* *Gregory P. Crawford,* and *Dirk J. Broer*

Alignment layers are extensively used in the production of liquid crystal displays (LCDs) in order to orient the liquid crystal molecule to give a desired optical effect.[1–6] For instance, planar alignment of liquid crystals—long axes of molecules in the plane of the substrate—is often enforced with specific polyimide layers, in combination with mechanical rubbing (buffing) procedure, producing unidirectional alignment that can propagate over macroscopic distances. Polyimides are usually preferred because of their excellent properties with respect to chemical resistance, thermal stability, adhesion

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