DOI: 10.1002/ejic.200800563

Cobalt and Copper Coordination Polymers Containing Acetylacetonato-Derived Ligands and Bidentate Pyridine Coligands: Synthesis, Crystal Structures and Magnetic Properties

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Dedicated to Prof. Loreto Ballester on the occasion of her retirement

Keywords: Chain structures / X-ray diffraction / Magnetic properties / N ligands / O ligands

One-dimensional chain derivatives of the general formula [M(acac)$_2$(μ-bipyridine)] were obtained from (acetylacetonato)cobalt(II) or (trifluoromethylacetylacetonato)copper(II) derivatives and bipyridine-like bridging ligands: 1,2-bis(4-pyridyl)ethane, 4,4′-bpa (**1**, Co; **2**, Cu), *trans*-1,2-bis(4-pyridyl)ethylene, 4,4′-bpe (**3**, Co; **4**, Cu), 1,2-bis(2-pyridyl)ethylene, 2,2′-bpe (**5**, Co) or pyrazine (**7**, Cu). The reaction of the copper parent derivative with 2,2′-bpe gives rise, however, to a dimeric species [{Cu(tfacac)$_2$}$_2$(μ-2,2′-bpe)] (**6**). Derivatives **4**–**7** were characterized by X-ray crystallography, which showed linear (**4**, **7**) or zigzag chains (**5**), depending on the bipyridine ligand shape. In the chain complexes, the metal centre is six-coordinate; the oxygen donor atoms of the acetylacetonato ligands occupy the equatorial positions and the bridging bipyridine ligands are in *trans* axial positions. Compound **6** forms a dimer with the two copper atoms in a square pyramidal environment, in which the nitrogen atoms of the bridging 2,2′-bpe ligand occupy the apical position in each pyramid. Magnetic susceptibility studies of the cobalt compounds are dominated by the spin–orbit coupling characteristic of this metal ion. At low temperatures and in the copper derivatives, weak antiferromagnetic interactions along the chain were observed.

Introduction

The use of unsaturated transition-metal coordination complexes and organic bidentate or multifunctional ligands as precursors to organic–inorganic hybrid materials is of considerable interest due to the diverse architectures and the potential properties of these materials, such as magnetic, nonlinear optic, catalysis and electronic properties.[1] The design and study of coordination polymers with specific network topologies can provide highly ordered networks with different dimensionalities; for example, linear or zigzag chains, two-dimensional sheets and three-dimensional networks have been described.[2] Generally, some control over the type and topology of the product generated from the self-assembly of inorganic metal species and organic ligands can be achieved by careful choice of the building blocks (metal complex and organic ligand), solvent system or metal-to-ligand ratio.[3]

In contrast, the unsaturated metal complexes [M(acetylacetonato)$_2$] are of interest as building blocks of supramolecular structures. Many examples of one-dimensional chain compounds connected by bidentate bridging ligands have been reported.[4] In particular, research has been concentrated on the use of pyrazine and 4,4′-bypiridine-based rod-like ligands.[5] In the last years, several crystalline polymers have been synthesized by using [M(acetylacetonato)$_2$] complexes (M = Co, Cu) and different bridging ligands, for example: [Co(acac)$_2$(μ-L)] (acac = acetylacetonato; L = pyrazine, 4,4′-bipyridine),[6] [Cu(tfacac)$_2$(μ-L)] (tfacac = trifluoromethylacetylacetonato, L = 4,4′-bipyridine),[7] [Cu(nbtfa)$_2$(μ-pyz)] [nbtfa = (*p*-nitrobenzoyl)trifluoromethylacetylacetonato],[8] [Cu(hfacac)$_2$(μ-L)] [hfacac = hexafluoroacetylacetonato; L = pyz; 4,4′-bipyridyl-*N*,*N*′-dioxide; 1,3-dipyridylpropane; 1,2-bis(3-pyridyl)ethyne; 1,2-bis(2-pyridyl)butadiyne; 1,2-bis(4-pyridyl)ethane][9] and [Co(hfacac)$_2$(μ-L)] (L = 4,4′-bipyridyl-*N*,*N*′-dioxide).[9b]

In this work we present the synthesis, crystal structures and magnetic properties of new cobalt(II) and copper(II) compounds formed by reaction of [Co(acac)$_2$] and [Cu(tfacac)$_2$] with different bidentate N-donor ligands (see Scheme 1): pyrazine (pyz), 1,2-bis(4-pyridyl)ethane (4,4′-bpa), *trans*-1,2-bis(4-pyridyl)ethylene (4,4′-bpe) and 1,2-bis(2-pyridyl)ethylene (2,2′-bpe). The used ligands possess different positions of the nitrogen atom and the spacer groups. The choice of the organic ligand is an important

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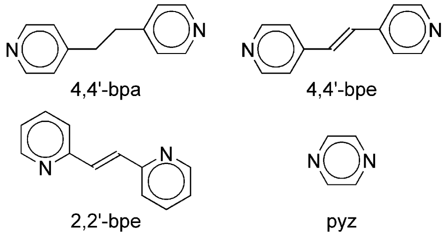
influence in determining the type and topology of the product. So, the properties of the ligand, such as, length, geometry, coordination ability and relative orientation of the donor groups, can play a very important role in dictating polymer topology and even in affecting the formation of polymer versus oligomer versus molecule.[10,11] In contrast, the comparative study of the reactions of [Cu(acac)$_2$] and [Cu(tfacac)$_2$] can show the different Lewis acidic character of the acetylacetonato complex used. It is noteworthy that very few complexes of [Cu(tfacac)$_2$] with N-donor bridging species have been reported.[7,10,11] Moreover, the fluorine atoms in [Cu(tfacac)$_2$] could promote a C–F···H–C hydrogen-bonding system, which could expand the one-dimensional chain structure into two-dimensional networks.[9e,12,13]



Scheme 1. Bridging ligands used in this work.

Results and Discussion

The new compounds were obtained by reaction of bis(acetylacetonato)cobalt or bis(trifluoromethylacetylacetonato)copper derivatives and the corresponding bipyridine or pyrazine in a 1:1 molar ratio. The copper derivatives crystallize from the reaction mixture, whereas the cobalt ones precipitate upon formation. When these reactions were carried out with unsubstituted bis(acetylacetonato)copper no reaction took place even when higher temperatures or reaction times were used. This fact can be explained by the lower Lewis acidic character of [Cu(acac)$_2$] relative to that of [Cu(tfacac)$_2$].

The general formula of the obtained compounds accounts for the one-dimensional polymeric form [Co(acac)$_2$(μ-L)] (L = 4,4′-bpa, **1**; 4,4′-bpe, **3**; 2,2′-bpe, **5**) or [Cu(tfacac)$_2$(μ-L)] (L = 4,4′-bpa, **2**; 4,4′-bpe, **4**; pyz, **7**). The use of different molar ratios of [M(acac)$_2$] to bipyridine ligand always led to the polymeric species. In contrast, the reaction of the parent copper derivative with 2,2′-bpe did not afford the polymeric species; instead, dimeric [{Cu(tfacac)$_2$}$_2$(μ-2,2′-bpe)] (**6**) was obtained.

Compound **6** was also obtained by electrochemical synthesis, in an attempt to obtain the polymeric-related species, by using a copper anode and a platinum cathode in a solution of trifluoromethylacetylacetone and 2,2′-bpe ligands in acetonitrile. The electrochemical efficiency for the process, E_f, defined as the number of mol of metal dissolved per faraday of charge, was close to 1. This value shows that the anodic oxidation leads initially to a Cu^{I} species, which is either oxidized to Cu^{II} later in solution or is disproportioned to Cu^{II} and Cu^{0}. This behaviour has already been observed in other systems, in which species of low-oxidation states are the initial electrochemical products.[14] The appearance of a copper metallic mirror on the walls of the electrochemical cell supports the latter process. This fact, along with the evolution of hydrogen at the cathode, suggests that the possible mechanism that takes place is that shown in Scheme 2. This type of synthesis was already shown to be quite effective in obtaining mixed complexes in a single step by simply adding a second ligand to the cell.[14]

cathode: $\text{tfacacH} + e^- \longrightarrow \text{tfacac}^- + 1/2\text{H}_2$

anode: $\text{Cu} + \text{tfacac}^- \longrightarrow [\text{Cu(tfacac)}] + e^-$

$4\,[\text{Cu(tfacac)}] + 2,2'\text{-bpe} \longrightarrow [\{\text{Cu(tfacac)}_2\}_2(\mu\text{-}2,2'\text{-bpe})] + 2\,\text{Cu}^0$

Scheme 2. Proposed mechanism for the electrochemical synthesis of **6**.

The IR spectra of these compounds confirm the chelation of the acetylacetonato groups by the presence of characteristic ν(C=O) bands at 1590–1645 cm^{-1} and ν(C–O) at 1460–1490 and 1260–1310 cm^{-1}.

The thermal analysis of the copper compounds show weight loss starting around 250 °C, which corresponds to the simultaneous decomposition of the parent derivative and sublimation of the remaining product, precluding any further interpretations. The cobalt derivatives, in contrast, show simultaneous loss of the bipyridine ligand and decomposition of the [Co(acac)$_2$] moiety to form cobalt oxide as the residue (84–91% weight loss depending on the parent derivative).

Crystal Structure of 4

This compound crystallizes in the space group $P\bar{1}$. Figure 1 shows the ORTEP view of the molecular unit.

The crystal structure is described as formed by one-dimensional chains of bis(trifluoromethylacetylacetonato)copper bridged by the bipyridine ligand. The copper atom, which is located on an inversion centre, shows a distorted octahedral environment surrounded by four oxygen atoms in the equatorial plane with bond lengths of 1.944(2) and 1.996(2) Å, and with two nitrogen atoms of the bridging groups in the axial positions at 2.375(3) Å, mainly due to the usual Jahn–Teller distortion in copper(II) complexes, showing similar features to those found in related species.[9] The bipyridine ligand in time is bonded to two [Cu(tfacac)$_2$] units, which gives rise to the formation of chains extending along the [101] crystal direction (Figure 2). The individual chains run parallel in the crystal and do not interact with each other except for a weak π–π interaction between C9 and C10 of a neighbouring chain at a distance of 3.396(6) Å.

The acetylacetonato ligand shows some disorder due to the presence of the trifluoromethyl group. The fluorine atoms are located either on C5, with an 80% occupancy, or

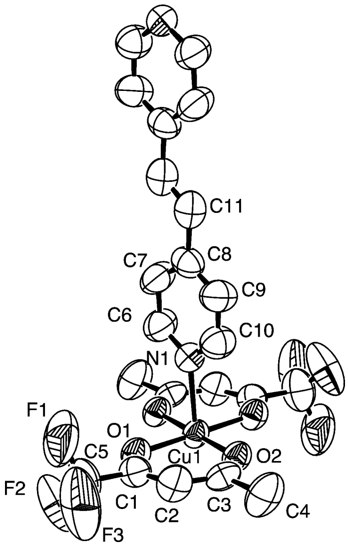


Figure 1. ORTEP view (50% probability ellipsoids) and labelling scheme of **4**. The disordered fluorine (see text) and the hydrogen atoms are omitted for clarity.

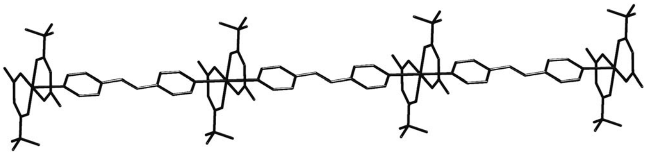


Figure 2. View of one chain in the crystal structure of **4**.

on C4, for the remaining 20%, alternating with the hydrogen methyl atoms. This disorder does not introduce any special features to the crystal packing.

Crystal Structure of 5

This compound crystallizes in the $P2_1/n$ group. Figure 3 shows a view of the asymmetric unit indicating the labelling scheme.

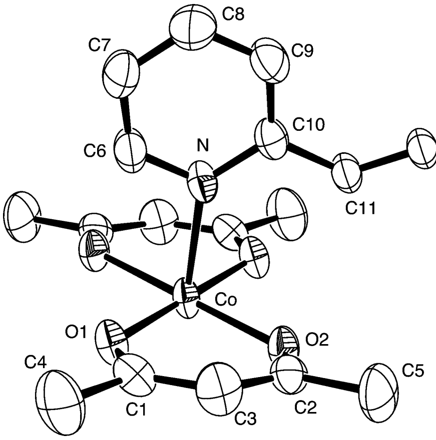


Figure 3. ORTEP view of **5** (50% probability ellipsoids).

As in the previous compound, the metal atom is located on an inversion centre and six-coordinate in an octahedral environment formed by four oxygen atoms of the two acetylacetonato ligands, which show bond lengths of 2.031(2) and 2.027(2) Å, and by two nitrogen atoms of two bipyridine groups, which occupy the *trans* positions at 2.292(2) Å. This longer distance reflects the Jahn–Teller distortion expected in a d^7 Co^{II} octahedral compound.

The bipyridine ligand bridges two [Co(acac)$_2$] moieties to give rise to the formation of chains running parallel to the *a* cell axis (Figure 4). The individual chains are isolated in the crystal, without significant interactions with the surrounding chains.

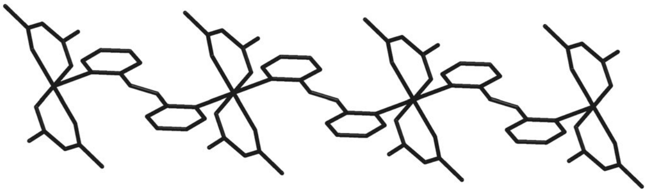


Figure 4. View of the polymeric zigzag chain formed in the crystal structure of **5**.

Crystal Structure of 6

This compound crystallizes in the space group $P\bar{1}$. Figure 5 shows the ORTEP view of the molecule.

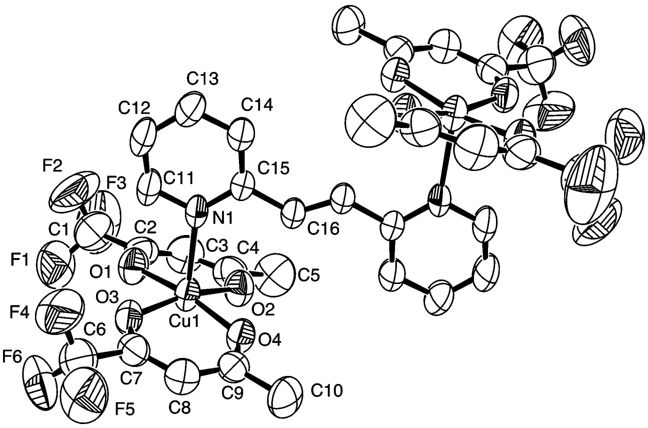


Figure 5. ORTEP view (50% probability ellipsoids) and labelling scheme of **6**. The disordered fluorine (see text) and the hydrogen atoms are omitted for clarity.

The molecular unit is a dimer formed by two [Cu(tfacac)$_2$] units bridged by one 2,2′-bpe ligand. Because the bridging ligand is located on an inversion centre, the asymmetric unit is composed of one copper atom, two trifluoromethylacetylacetonato ligands and half of the bipyridine ligand.

The coordinative environment of the copper atom is square pyramidal; the four oxygen atoms of the acetylacetonato ligands form the square base at a mean distance of 1.934 Å and one pyridine nitrogen at 2.315(3) Å occupies the apical position. The copper atom is located 0.212(1) Å above the pyramid basal plane, as expected in a five-coordinate environment.

The trifluoromethyl groups in the acetylacetonato ligands show some disorder, in a way similar to that described for **4**, alternating in the two methyl positions of both acetylacetonato groups of the asymmetric unit with approximate relative occupancies of 2/3 and 1/3.

Crystal Structure of 7

This compound crystallizes in the *C*2/*m* space group. Figure 6 shows the ORTEP view of the molecular unit.

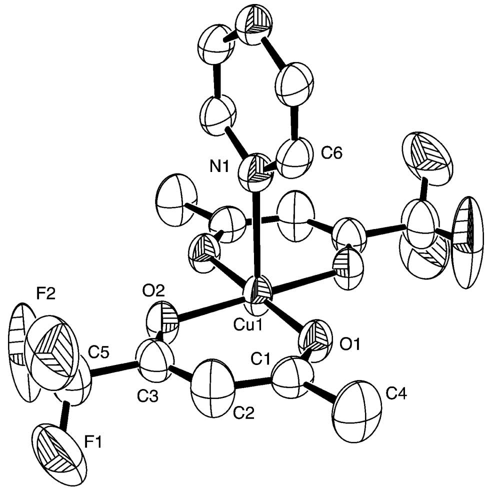


Figure 6. ORTEP view (50% probability ellipsoids) and labelling scheme of **7**. The disordered fluorine (see text) and the hydrogen atoms are omitted for clarity.

The crystal structure is composed of [Cu(tfacac)$_2$] units bridged by pyrazine ligands to form one-dimensional chains running along the *b* crystal axis (Figure 7). The copper atom is located on the inversion centre, and the two pyrazine nitrogen atoms lie on the twofold axis, whereas the acetylacetonato groups lie on the mirror plane. Therefore, the asymmetric unit corresponds to one trifluoromethylacetylacetonato ligand chelated to the copper atom and one quarter of the pyrazine ligand. The copper atom is six-coordinate in the usual Jahn–Teller elongated octahedron with one basal plane formed by the four oxygen atoms of two acetylacetonato ligands, bonded at distances of 1.931(2) and 1.965(2) Å, whereas the nitrogen atoms of the bridging pyrazine are located at 2.510(3) Å above and below this equatorial plane.

The chains are closely packed by opposing the bis(acetylacetonato)copper moiety of one chain to the pyrazine groups of the surrounding chains. The only interatomic interaction found between adjacent chains corresponds to a short contact between F1 of one trifluoromethyl group and H4B/H4C of neighbouring methyl groups of the next chain with a distance of 2.22(1) Å. These interactions run parallel to the chain main axis, and because the two tfacac ligands of every copper atom link different chains, they extend the interactions in a three-dimensional way along the whole crystal.

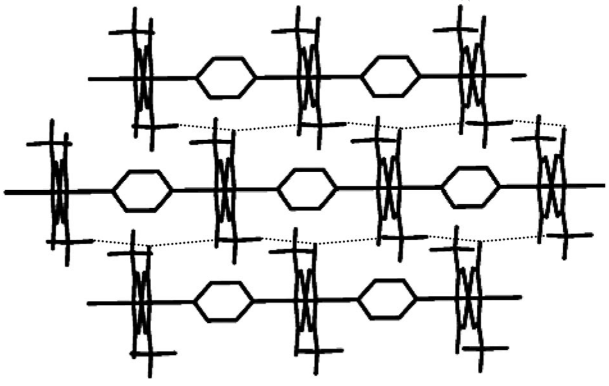


Figure 7. View of the polymeric chains formed in the crystal structure of **7**, showing, as dotted lines, the C–F···H–C intermolecular short contacts.

Magnetic Properties

The magnetic susceptibilities of the compounds were measured in the temperature range 2–300 K. The magnetic moments of copper derivatives **2**, **4**, **6** and **7** follow the Curie law above 20 K with magnetic moments $\{g[S(S+1)]^{1/2}\}$ ranging from 1.66 to 2.10 β (χT = 0.34–0.55 cm^3 K mol^{-1}) typical for isolated S = 1/2 spins. The magnetic moment decreases below this temperature in an indication of small antiferromagnetic exchange interactions between neighbouring copper atoms. Because the structures of compounds **2**, **4** and **7** correspond to one-dimensional chains, the copper–copper antiferromagnetic interactions were fitted to an isotropic Heisenberg one-dimensional chain model on the basis of the exchange Hamiltonian, $H = -J\Sigma S_iS_{i+1}$, were J is the exchange coupling constant for the copper ions.[15] Figure 8 shows the temperature dependence of χT for compound **7**, chosen as a representative example. The best-fitting values correspond to g_{Cu} = 2.19 and J = –0.12 cm^{-1} for compound **2**, g_{Cu} = 1.92 and J = –0.18 cm^{-1} for **4** and g_{Cu} = 2.21 and J = –0.13 cm^{-1} for **7**. The low J values indicate that the antiferromagnetic exchange between copper atoms is almost negligible, as expected from the long metal–metal distances found in the crystals. In addition, the π-bridging pyridine systems are always coordinated in

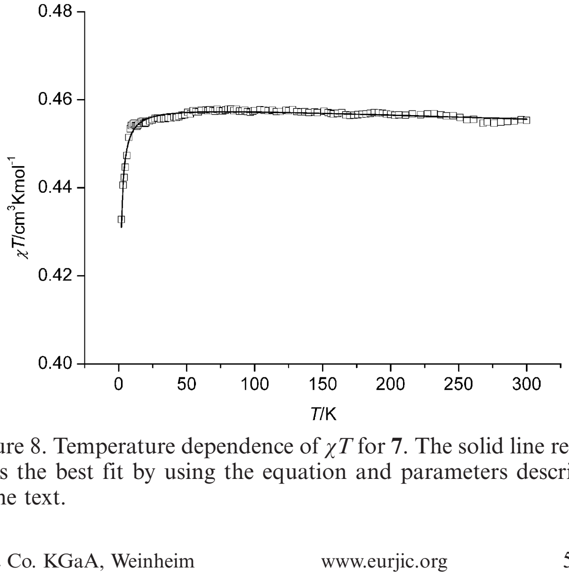


Figure 8. Temperature dependence of χT for **7**. The solid line represents the best fit by using the equation and parameters described in the text.

apical positions, perpendicular to the unpaired copper electron, thus avoiding any possible magnetic pathway.

Compound **6** forms dimers, and the magnetic data are interpreted on the basis of the general isotropic exchange Hamiltonian for two interacting $S = 1/2$ spins, $H = -JS_1S_2$.[16] The best fit, $g_{\mathrm{Cu}} = 2.41$, $J = -0.15\ \mathrm{cm}^{-1}$, also indicates the presence of a very weak exchange interaction between neighbouring coppers, as the similar bridging ligand keeps the copper atoms away and no intermolecular short contacts were found in the crystal structure.

The magnetic moments of the cobalt derivatives continuously decrease from 4.7–5.1 β ($\chi T = 2.8$–$3.2\ \mathrm{cm^3\,K\,mol^{-1}}$) at 300 K to 3.2–3.5 β ($\chi T = 1.3$–$1.5\ \mathrm{cm^3\,K\,mol^{-1}}$) at 5 K. Because the theoretical spin-only value corresponds to 3.8 β, we expect an important orbital contribution in all cases.[17,18] The plots of χT vs. T (Figure 9) for compounds **1**, **3** and **5** show a change in the slope at 20 K in the three cases. From this point, the observed decrease in the magnetic moment from the spin-only value on cooling can be interpreted as the effect of a small antiferromagnetic coupling between the cobalt centres, similar to that described above for the copper chains.

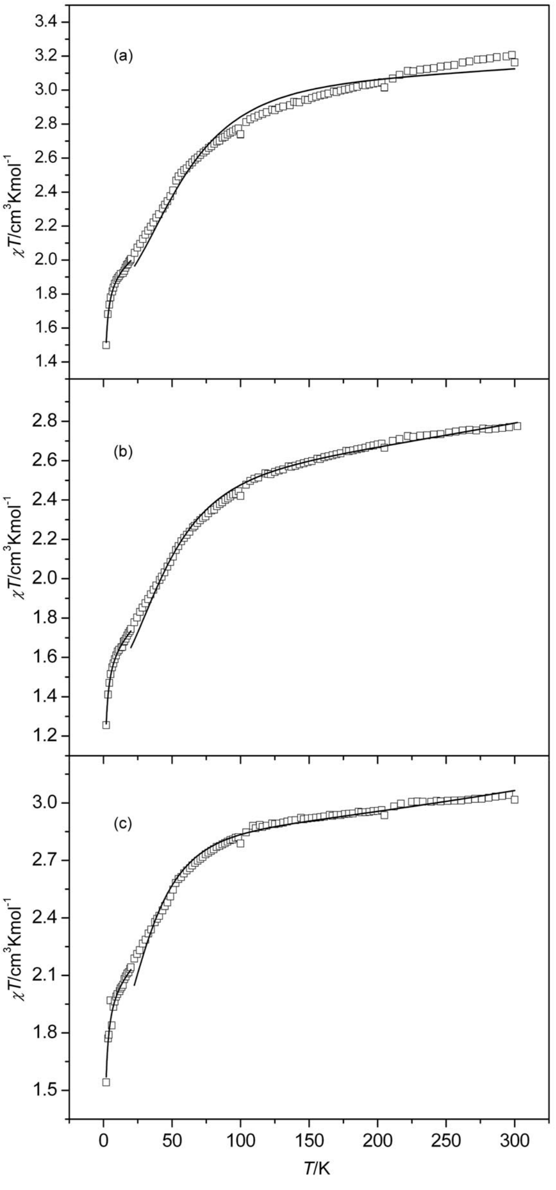


Figure 9. Temperature dependence of χT for **1** (a), **3** (b) and **5** (c). In all cases the solid lines represent the best fit of the experimental data as described in the text.

For this reason, we have fitted the data between 5 and 20 K for the three compounds to the Curie–Weiss law for $S = 3/2$ spin and obtained a coupling constant for the antiferromagnetic interaction from the Weiss constant by using the expression $\theta = zJS(S + 1)/3k_B$, where z is the number of interacting spins and is assumed to be 2, considering that the interaction is transmitted along the chain. The best fit in every case, $g_{\mathrm{Co}} = 2.03$ and $J = -0.16\ \mathrm{cm}^{-1}$ for **1**, $g_{\mathrm{Co}} = 1.91$ and $J = -0.18\ \mathrm{cm}^{-1}$ for **3** and $g_{\mathrm{Co}} = 2.09$ and $J = -0.18\ \mathrm{cm}^{-1}$ for **5**, affords coupling constant values of the same order as those found for the analogous copper compounds.

Above 20 K, the data were fitted by using the magnetic formula given by Mabbs[18] and Miller[19] for a mononuclear Co$^{\mathrm{II}}$ complex by calculating the λ value (spin–orbit coupling parameter) and the a parameter ($a = 1.5$ in the limit of small field) and by considering that the antiferromagnetic coupling between neighbouring spins is negligible. The best-fit parameters are $\lambda = -154\ \mathrm{cm}^{-1}$ and $a = 1.5$ for **1**, $\lambda = -161\ \mathrm{cm}^{-1}$ and $a = 1.43$ for **3** and $\lambda = -154\ \mathrm{cm}^{-1}$ and $a = 1.49$ for **5**. The λ parameters appear in the range observed for similar complexes[20] and are close to the expected value for an isolated Co$^{\mathrm{II}}$ ion ($-175\ \mathrm{cm}^{-1}$);[18] the difference can be explained in terms of the covalence in the cobalt complexes.

Conclusions

New one-dimensional derivatives of copper and cobalt were synthesized. These complexes are based on [M(acac)$_2$] square-planar moieties bridged by bipyridine ligands occupying the apical positions, which gives rise to a pseudooctahedral environment around the metal atom. The bipyridine ligand separates the paramagnetic metal centres, which allows only small antiferromagnetic couplings along the chain. The presence of asymmetric trifluoromethyl groups in the acetylacetonato ligand does not influence the properties of the studied compounds. The shape of the bipyridine ligand orientates the [M(acac)$_2$] units to form either linear or zigzag polymeric chains.

In contrast to the rest of the species described, compound **6** corresponds to a dimer formed by two [Cu(tfacac)$_2$] units linked by one 2,2′-bpe ligand, which leaves an square pyramidal environment for the metal atom. The long distance between the copper atoms, imposed by the size of the bridging ligand, is responsible, as before, for the small couplings observed between the unpaired spins.

Experimental Section

Physical Measurements: Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. Infrared spectra were recorded as KBr pellets with a Nicolet Magna-550 FTIR spectrophotometer. Magnetic experiments were made on polycrystalline samples by using a SQUID magnetometer MPMS-XL-5 manufactured by Quantum Design. The temperature dependence of the magnetization in the range between 2 and 300 K was recorded by using a constant magnetic field of 0.5 T. The experimental data were corrected for the magnetization of the sample holder (gelatine) and for atomic diamagnetism, as calculated from the known Pascal's constants. The thermogravimetric data were obtained with a Perkin–Elmer Pyris 1 TGA by using an open pan, which was purged with N_2, and at a heating rate of 10 °C min^{-1}.

Crystallographic Studies: Good quality crystals of **4**, **5**, **6** and **7** were obtained by slow diffusion of diluted solutions of the reactants. A summary of the fundamental crystal data is given in Table 1. The crystal data were collected in the "CAI de Difracción de Rayos X, UCM". In most cases, a green (orange for **5**) crystal was resin epoxy coated and mounted on a Bruker Smart CCD diffractometer by using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) operating at 50 kV and 25 mA. Data were collected over a reciprocal space hemisphere by combination of three exposure sets. Each frame exposure time was 20 s covering 0.3° in ω. The cell parameters were determined and refined by least-squares fit of all reflections collected. The first 50 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. No absorption corrections were applied. All the structures were solved by direct methods and refined by applying full-matrix least-squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. All calculations were carried out with the SHELX97 software package.[21] CCDC-690040 (for **4**), -690041 (for **5**), -690042 (for **6**) and -690043 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Co(acac)$_2$(μ-4,4′-bpa)] (1): A solution of 4,4′-bpa (0.092 g, 0.5 mmol) in ethanol (5 mL) was added to a stirred solution of [Co(acac)$_2$(H$_2$O)$_2$] (0.145 g, 0.5 mmol) in a mixture of ethanol (5 mL) and chloroform (5 mL). The mixture was stirred for 1 h to afford an orange precipitate of **1** (0.181 g, 82%). IR (KBr): ṽ = 3028 (w), 2992 (w), 2926 (w), 1592 (vs), 1557 (m), 1514 (s), 1465 (vs), 1409 (vs), 1253 (m), 1217 (w), 1198 (m), 1074 (w), 1069 (w), 1013 (s), 921 (s), 870 (w), 813 (w), 767 (s), 651 (m), 553 (m), 542 (m), 527 (m), 495 (w), 412 (m) cm^{-1}. $C_{22}H_{26}CoN_2O_4$ (441.39): calcd. C 59.86, H 5.94, N 6.35; found C 59.66, H 5.98, N 6.31.

[Cu(tfacac)$_2$(μ-4,4′-bpa)] (2): A solution of 4,4′-bpa (0.092 g, 0.5 mmol) in chloroform (5 mL) was added to a stirred solution of [Cu(tfacac)$_2$] (0.184 g, 0.5 mmol) in a mixture of ethanol (8 mL) and chloroform (8 mL). The mixture was stirred for 1 h, during which time the colour of the solution changed from blue to bright green. The solution was then cooled to 0 °C for 3 d to afford green crystals of **2** (0.215 g, 78%). IR (KBr): ṽ = 3050 (w), 1642 (vs), 1617 (s), 1568 (m), 1560 (s), 1491 (s), 1431 (m), 1358 (w), 1283 (vs), 1221 (m), 1185 (s), 1127 (vs), 1075 (w), 1027 (w), 925 (w), 885 (m), 818 (w), 771 (m), 751 (w), 728 (m), 669 (w), 566 (m), 548 (m), 515 (w), 414 (w) cm^{-1}. $C_{22}H_{20}CuF_6N_2O_4$ (553.95): calcd. C 47.70, H 3.64, N 5.06; found C 47.89, H 3.47, N 5.17.

[Co(acac)$_2$(μ-4,4′-bpe)] (3): A solution of 4,4′-bpe (0.091 g, 0.5 mmol) in chloroform (5 mL) was added to a stirred solution of [Co(acac)$_2$(H$_2$O)$_2$] (0.145 g, 0.5 mmol) in a mixture of ethanol (5 mL) and chloroform (5 mL). An orange precipitate immediately formed, and the mixture was stirred for 1 h our, after which orange solid **3** (0.211 g, 95%) was collected. IR (KBr): ṽ = 3056 (w), 2985 (w), 2916 (w), 1602 (vs), 1558 (w), 1514 (s), 1460 (s), 1411 (s), 1349 (m), 1257 (m), 1210 (w), 1193 (w), 1094 (w), 1073 (w), 1010 (m), 993 (m), 920 (m), 837 (m), 762 (m), 653 (w), 554 (s), 410 (m) cm^{-1}. $C_{22}H_{24}CoN_2O_4$ (439.37): calcd. C 60.14, H 5.51, N 6.38; found C 59.94, H 5.49, N 6.40.

[Cu(tfacac)$_2$(μ-4,4′-bpe)] (4): A solution of 4,4′-bpe (0.091 g, 0.5 mmol) in chloroform (7 mL) was added to a stirred solution of [Cu(tfacac)$_2$] (0.184 g, 0.5 mmol) in a mixture of ethanol (8 mL) and chloroform (8 mL). The mixture was stirred for 1 h and cooled to 0 °C for 3 d to afford green crystals of **4** (0.156 g, 57%). IR

Table 1. Crystal and refinement data for compounds **4**–7.

	4	**5**	**6**	**7**
Empirical formula	$C_{22}H_{18}CuF_6N_2O_4$	$C_{22}H_{24}CoN_2O_4$	$C_{16}H_{13}CuF_6NO_4$	$C_{14}H_{12}CuF_6N_2O_4$
Formula mass	551.92	439.36	460.81	449.80
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/m$ (No. 12)
a / Å	8.5384(9)	8.3143(9)	8.945(1)	10.6443(17)
b / Å	8.9181(9)	7.8882(9)	10.9994(13)	7.8218(12)
c / Å	9.1121(9)	16.7397(18)	11.7571(14)	11.2109(18)
α / °	63.155(2)	90	112.619(2)	90
β / °	73.639(2)	98.421(2)	109.806(2)	111.566(3)
γ / °	82.850(2)	90	98.540(2)	90
V / Å^3	594.0(2)	1086.0(2)	951.4(3)	868.0(2)
Z	1	2	2	2
$\rho_{\text{calcd.}}$ / Mg m^{-3}	1.543	1.344	1.609	1.721
μ / mm^{-1}	0.997	0.819	1.226	1.342
θ range / °	2.49–29.06	2.46–28.84	2.08–28.78	1.95–28.72
Reflections collected	5734	6762	6137	2815
Independent reflections	2750	2571	4336	1112
Refined parameters	187	135	308	91
Goodness of fit	0.872	0.780	0.791	1.019
R_1[a] $[I > 2\sigma(I)]$	0.0465	0.0384	0.0436	0.0376
wR_2[b] $[I > 2\sigma(I)]$	0.1035	0.0785	0.0905	0.0931

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

(KBr): $\tilde{\nu}$ = 3049 (w), 1620 (vs), 1603 (s), 1560 (m), 1523 (s), 1482 (s), 1421 (m), 1363 (m), 1299 (s), 1228 (m), 1192 (s), 1135 (vs), 1001 (m), 987 (m), 862 (m), 832 (s), 773 (s), 730 (m), 586 (m), 554 (s), 432 (w) cm^{-1}. $C_{22}H_{18}CuF_6N_2O_4$ (551. 93): calcd. C 47.88, H 3.28, N 5.08; found C 47.95, H 3.16, N 5.18.

[Co(acac)$_2$(μ-2,2′-bpe)] (5): A solution of 2,2′-bpe (0.091 g, 0.5 mmol) in chloroform (4 mL) was added to a stirred solution of [Co(acac)$_2$(H$_2$O)$_2$] (0.145 g, 0.5 mmol) in a mixture of ethanol (4 mL) and chloroform (4 mL). The solution was stirred for 1 h and cooled to 0 °C for 3 d to afford orange crystals of **5** (0.146 g, 66%). IR (KBr): $\tilde{\nu}$ = 3086 (m), 3068 (w), 2988 (w), 2957 (m), 2916 (w), 1594 (vs), 1565 (m), 1518 (s), 1460 (vs), 1408 (vs), 1357 (s), 1278 (w), 1262 (s), 1220 (m), 1198 (m), 1162 (m), 1093 (w), 1063 (m), 1013 (m), 1003 (m), 979 (s), 925 (s), 784 (m), 770 (s), 749 (s), 652 (m), 634 (m), 572 (m), 555 (m), 539 (s), 499 (m), 413 (s) cm^{-1}. $C_{22}H_{24}CoN_2O_4$ (439.37): calcd. C 60.14, H 5.51, N 6.38; found C 60.19, H 5.59, N 6.33.

[{Cu(tfacac)$_2$}$_2$(μ-2,2′-bpe)] (6): A solution of 2,2′-bpe (0.091 g, 0.5 mmol) in chloroform (4 mL) was added to a stirred solution of [Cu(tfacac)$_2$] (0.184 g, 0.5 mmol) in a mixture of ethanol (4 mL) and chloroform (4 mL). The mixture was stirred for 1 h, and the solvent was left to evaporate for 24 h to afford green crystals of **6** (0.215 g, 47%). IR (KBr): $\tilde{\nu}$ = 3090 (w), 3028 (w), 1637 (m), 1612 (vs), 1568 (m), 1530 (s), 1480 (s), 1444 (m), 1365 (m), 1306 (vs), 1227 (s), 1196 (s), 1138 (vs), 1057 (w), 1025 (w), 1006 (m), 976 (m), 949 (m), 864 (m), 789 (s), 760 (w), 750 (m), 733 (m), 623 (m), 591 (s), 536 (w), 517 (w), 496 (w), 435 (w), 412 (w) cm^{-1}. $C_{32}H_{26}Cu_2F_{12}N_2O_8$ (921.63): calcd. C 41.70, H 2.84, N 3.04; found C 41.82, H 2.85, N 3.12.

Electrochemical Synthesis of [{Cu(tfacac)$_2$}$_2$(μ-2,2′-bpe)] (6): The electrochemical procedure used in this synthesis was similar to that described by Tuck and coworkers.[22] The cell was a tall-form beaker (100 mL) fitted with a rubber bung, through which the electrochemical leads entered the cell. The anode was a copper wire and the cathode was a platinum wire. The electrolysis of an acetonitrile solution (60 mL) containing trifluoromethylacetylacetone (0.628 g, 4 mmol), 2,2′-bpee (0.367 g, 2 mmol) and tetrabutylammonium tetrafluoroborate (0.015 g, mmol) as supporting electrolyte by using a d.c. current of 15 V and 50 mA for 2 h and 10 min dissolved 0.25 g of copper ($E_f \approx 1$ mol F^{-1}). Gaseous nitrogen was bubbled through the solution during reaction time. During the electrolysis, hydrogen was evolved at the cathode, the colour of the solution changed from colourless to green and a deposit of copper metal was formed at the bottom and on the walls of the vessel and on the cathode. The cell can be summarized as follow: Pt(–)/CH$_3$CN + tfacacH + 2,2′-bpee/Cu(+). At the end of the experiment, the reaction mixture was filtered, and the filtrate was kept at room temperature for 5 d to afford green crystals of **6**. The solid obtained was filtered, washed with diethyl ether and several times with methanol and dried under vacuum (0.75 g, 82.8%).

[Cu(tfacac)$_2$(μ-pyz)] (7): A solution of pyrazine (0.040 g, 0.5 mmol) in chloroform (4 mL) was added to a stirred solution of [Cu(tfacac)$_2$] (0.184 g, 0.5 mmol) in a mixture of ethanol (4 mL) and chloroform (4 mL). The mixture was stirred for 1 h and cooled to 0 °C for 3 d to afford green crystals of **7** (0.095 g, 42%). IR (KBr): $\tilde{\nu}$ = 3036 (w), 1622 (vs), 1550 (m), 1520 (s), 1471 (s), 1434 (m), 1403 (m), 1362 (m), 1300 (vs), 1227 (s), 1202 (s), 1135 (vs), 1071 (w), 1034 (m), 1023 (m), 925 (w), 861 (m), 800 (m), 773 (m), 732 (m), 620 (m), 587 (m), 519 (w), 440 (s) cm^{-1}. $C_{14}H_{12}CuF_6N_2O_4$ (449.80): calcd. C 37.38, H 2.69, N 6.23; found C 37.30, H 2.58, N 6.13.

Acknowledgments

We gratefully acknowledge the Spanish Ministerio de Educación y Ciencia (project MAT2006-05417) and the Comunidad Autónoma de Madrid (project S0505-PPQ-0316) for financial support.

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Received: June 4, 2008