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Self-Organized Metallo-Helicates and -Ladder with 2,2′-Biphenyldicarboxylate $(C_{14}H_8O_4)^{2-}$: Synthesis, Crystal Structures, and Magnetic Properties

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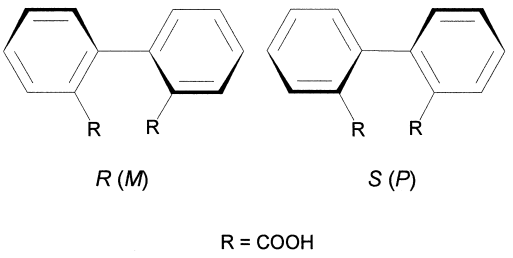
We report on the hydrothermal synthesis, single-crystal structures and magnetic properties of three one-dimensional coordination polymers employing the 2,2′-biphenyldicarboxylate dianion, $(C_{14}H_8O_4)^{2-}$, as the bridging component. $[M^{II}(H_2O)_4(C_{14}H_8O_4)]$, where M = Co (**1**) and Ni (**2**), consist of helical chains of square-planar $M^{II}(H_2O)_4$ bridged by $C_{14}H_8O_4$ with each carboxylate group acting as a mono-dentate ligand. The magnetic properties are those of paramagnets (**1**: $C = 3.34(1)$ cm^3 K/mol, $\mu_{\rm eff} = 5.17\ \mu_B$, $\theta = -51(1)$ K; **2**: $C = 0.985(9)$ cm^3 K/mol, $\mu_{\rm eff} = 2.81\ \mu_B$, $\theta = +27(2)$ K) with an antiferromagnetic exchange for **1** and a ferromagnetic exchange for **2**. $Cu_2(C_{14}H_8O_4)(H_2O)_2$ (**3**) is composed of tetracarboxylato-dimeric units bridged into ladders by biphenyl units. The ladders are packed parallel to each other, and narrow channels are present due to insufficient space filling of the biphenyl rings. Its magnetic behavior follows that of a Bleaney–Bowers singlet-triplet model with a gap of 470(10) K.

Coordination polymers are attracting much interest due to the strength and rigidity of the extended lattices for gas sorption and intercalation and for the connectivity between magnetic ions in designing molecular magnets.[1–5] They belong to a subset of organic–inorganic hybrid materials, and usually employ a central metal ion and a multitopic organic ligand or a coordination complex having ambidentate ligands, such as cyanide and oxalate.[6–9] In some cases, other organic ligands are used to control the dimensionality or structure.[10,11] The choice of the metals and of the ligands depends on the desired properties. On the one hand, there is strong interest by scientists studying catalysis and the adsorption of gases originating from the possibility of creating structures with cavities, channels or pores and, consequently, large surface areas.[12–15] On the other hand, there is increasing interest from magneto-chemists due principally to the realization of organizing the magnetic orbitals of the moment carriers to favor a particular magnetic ground state.[3,4,6–8,16] One good and simple example of the latter is the use of the dicyanamide $(N(CN)_2{}^-)$ ion to organize divalent transition metals into a 3-dimensional coordination polymer having a Rutile-like structure.[17–19] The ligand does not have to be diamagnetic, as in the case of dicyanamide. The field of coordination polymers based on organic radicals is a very active area, indeed.[20–24] Several ground states have been established and a clear molecular-orbital picture to explain the observations is emerging.[3,4,25] Our present interest in the field of molecular magnetism resides in the use of small diamagnetic ligands; recently, we are making use of the coordination properties of the carboxylate ion.[26]

The key to designing polymeric structures is, in general, that employed in the field of supra-molecular chemistry; further, all of the rules of covalent and hydrogen bonding are also adopted.[27,28] Over the last decade the choice of ligands has evolved from the traditional simple cyanide, thiocyanate, nitrate, nitrite, and oxalate to more unconventional, complex and large ligands, such as the poly-pyridines, poly-amines and polycyanides, which have structure-directive properties through their geometry and stereochemistry.[5,10,11,29–31] The polycyanides provide another factor in complexity, that of electrical conductivity. A very good example, which has been thoroughly studied, is $Cu(DCNQI)_2$ and its analogues, because they exhibit a range of interesting cooperative phenomena, such as charge redistribution, π–d interaction, electronic conduction, metal–insulator transition, superconductivity, and weak ferromagnetism.[32] The use of functionalized TTF is also being developed. Several examples of poly-phosphates, -phosphinates and carboxy-phosphonates are known. Poly-carboxylates have so far been principally used by those interested in gas sorption.[1,13,15] Following the disappointing, though very interesting, early work on using poly-carboxylate to propagate magnetic exchange, we recently found some interesting magnetic properties from compounds containing mono-carboxylates, di-carboxylates, tri-carboxylates, and a tetracarboxylate.[26,33] Their magnetic properties range from ferrimagnetic with Curie temperatures of up to 60 K and a coercivity of 20 kOe to metamagnetic with remanance and coercivity in excess of 50 kOe at 2 K.[26] In the present study we used 2, 2′-biphenyldicarboxylic acid (also known as diphenic acid, and abbreviated here as DPhA,) because it contains two sterically hindered carboxylate groups and adopts two optically active geometries (Scheme 1). Here, we report on the hydrothermal synthesis and structures of cobalt and nickel complexes that consist of helical chains, and of a copper complex that consists of copper dimers bridged into parallel ladders. We also report on their magnetic properties.



Scheme 1. Molecular structure of the *P* and *M* forms of diphenic acid.

Experimental

The syntheses were carried out in home-built teflon-lined cylindrical stainless-steel pressure bombs having a maximum capacity of 120 mL. X-ray powder diffraction data were collected using a Bragg–Bretano geometry on a Seimens D-500 with Co-$K\alpha$ (1.789 Å) radiation at room temperature. Thermogravimetric analyses (20 °C to 900 °C) were performed on a SETARAM TG-DTA system at a warming rate of 5 °C/minute in a constant flow of air. Infrared spectra were recorded by transmission through fine particles of the compounds dispersed on a KBr plate. The temperature and field dependence of the magnetization of the complexes were determined on a Quantum Design MPMS-XL SQUID operating in the temperature range 2 – 300 K and fields of up to 5 T.

All chemicals were obtained from Aldrich and Fluka, and were used without purification.

Preparation of [M^{II}(DPhA)(H_2O)$_4$], M = Co or Ni. Metal(II) nitrate hexahydrate (1 g), diphenic acid (0.5 g), and NaOH (0.34 g) were dissolved in distilled water (30 mL). The mixtures were placed in the Teflon liner of autoclaves, sealed and heated to 120 °C for 1 day. They were allowed to cool to room temperature in a water bath. In the case of cobalt, a black residue of cobalt oxide was formed together with red block crystals (yield 60%). The crystals were separated by decantation. For nickel, pale blue-green crystals were obtained from a clear solution. The crystals were washed with water and acetone and dried in air.

Calcd for **1**: $C_{14}H_{16}CoO_8$; C, 45.30; H, 4.34; Co, 15.88%; Found: C, 45.04; H, 4.33; Co, 15.84%.

Calcd for **2**: $C_{14}H_{16}NiO_8$; C, 45.33; H, 4.35; Ni, 15.83%; Found: C, 45.05; H, 4.34; Ni, 15.52%.

Preparation of [Cu^{II}_2 (DPhA)$_2$(H_2O)$_2$]. Copper(II) nitrate trihydrate (1 g) and diphenic acid (0.5 g) were dissolved in distilled water (30 mL). The mixtures were placed in the Teflon liner of autoclaves, sealed and heated to 120 °C for 1 day. The bomb was allowed to cool to room temperature in a water bath. Blue crystals were obtained from a clear solution (yield 65%). The crystals were washed with water and acetone, and dried in air.

Calcd for **3**: $C_{28}H_{20}Cu_2O_{10}$; C, 52.26; H, 3.13%; Found: C, 53.28; H, 3.18%.

X-ray Crystallography and Structure Solution. Selected single crystals were glued on the tip of glass fibers. Diffraction data for the complexes were collected on a Bruker SMART APEX CCD area detector employing the ω-scan mode at room temperature. The diffractometer was equipped with graphite-monochromated Mo-$K\alpha$ (0.7107 A) radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[34] The non-hydrogen atoms were refined anisotropically. The final cycle of a full-matrix least-squares refinement was based on the number of observed reflections and n variable parameters. They converged (a large parameter shift was σ times its e.s.d.) with agreement factors of $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w\,|F_o|^2]^{1/2}$. No extinction corrections were applied. Details of the crystallographic data are given in Table 1. The CIF data for the two crystals are deposited as Document No. 75028 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data hae been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 178288 – 178290.

Results and Discussion

Biphenyls containing large groups in the ortho-positions cannot freely rotate about the central bond because of a steric hindrance. This restricted rotation gives rise to perpendicular disymmetric planes and, consequently, two forms (*M* and *P*)

Table 1. Summary of Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
Formula	$C_{14}H_{16}CoO_8$	$C_{14}H_{16}NiO_8$	$C_{28}H_{20}Cu_2O_{10}$
Molecular weight	371.21	370.98	643.55
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$ (14)	$P2_1/n$ (14)	*Cmca* (64)
a/Å	14.347(1)	14.304(1)	21.224(3)
b/Å	7.5253(6)	7.4861(6)	7.045(1)
c/Å	15.578(1)	15.570(1)	17.720(3)
β/°	115.382(1)	115.756(1)	
V/Å^3	1519.6(2)	1501.6(2)	2649.4(7)
Z	4	4	4
D_c/g cm^{-3}	1.622	1.641	1.613
μ(Mo $K\alpha$)/cm^{-1}	11.69	13.32	16.64
No. unique Reflections	3752	3678	1584
No. observations	2326 ($I > 3.0\sigma(I)$)	2296 ($I > 3.0\sigma(I)$)	1584 (all data)
R (R_w)	0.035 (0.032)	0.034 (0.031)	0.043 ($2.0\sigma(I)$)
Residual (e$^-$/Å^3)	+0.47	+0.52	+0.64
	−0.46	−0.36	−0.75

(Scheme 1). An example is biphenyl 2,2′-disulfonic acid.[35] The case of hexahelicene is similar, in which one side must lie above the other because of crowding.[36] A literature search for biphenyldicarboxylate and binaphtyldicarboxylate revealed several examples of clathrates but, surprisingly, no crystallograhically characterized known examples of metal complexes.[37]

Synthesis. For the synthesis we employed a commercially available racemic mixture of two enantiomers of 2, 2′-biphenyldicarboxylic acid. Consequently, the resulting compounds consisted of equal amounts of the two forms. In **1** and **2**, we find that the structure consists of segregated helices (*M* and *P*), where each helix contains one form of the acid. Further details are given below. Hydrothermal reactions with transition metals in mild alkaline solutions with carboxylic acid usually give several phases, depending on the pH, the temperature, the concentration and sometimes the period of the reaction. Here, we repeatedly found good-quality crystals having a maximum size of 5 mm of only one phase under the conditions described above, while non-characterized forms were obtained as powders at higher pH and higher temperatures.

Structures of 1 and 2. X-ray crystal structure analyses of **1** and **2** revealed that the complexes are isostructural (Table 1) and show the expected lattice contraction on going from divalent cobalt with an ionic radius of 0.89 Å to nickel with 0.83 Å. The crystals belong to the monoclinic system, $P2_1/n$, a = 14.347(1), b = 7.5253(6), c = 15.578(1) Å, β = 115.382(1)°, V = 1519.6(2) Å^3 and Z = 4 for **1** and a = 14.304(1), b = 7.4861(6), c = 15.570(1) Å, b = 115.756(1)°, V = 1501.6(2) Å^3 and Z = 4 for **2**. Since the two compounds are isostructural, we restrict our description to only the cobalt compound, and only mention the pertinent points for nickel when appropriate. Figure 1 shows the asymmetric unit which contains one metal ion, one acid and four water molecules together with the atomic numbering scheme; selected bond distances and angles are given in Table 2. The key feature of the structure is one-dimensional helices consisting of pseudo square-planar $M(H_2O)_4$ units bridged by the dicarboxylate (Figs. 2 and 3). This structural feature is basically the same as those of other $M(H_2O)_4$-dicarboxylate, where the dicarboxylate is succinate, fumarate, or adipate.[38–40] The main difference is that in the alkane or alkene backbone the chains are linear, but in the present case of diphenic acid the chains are helical as a consequence of a restricted rotation of the acid mentioned above.

The geometry of the dianion in the present compounds is similar to those found in the pure acid.[41] The two phenyl rings are arranged in a near-orthogonal way, and appear like the wings of a butterfly. The carboxylate groups are slightly out of the plane of the phenyl rings. The average dihedral angles of the two CO_2 groups and the C_6 rings are 40° and 26°. The dihedral angle between the two carboxylate groups is 49°. The O···O distances within the CO_2 group are 2.19 and 2.235 Å. The distances (O···O) between the two CO_2 groups are 3.425, 3.772, 5.228 and 5.425 Å.

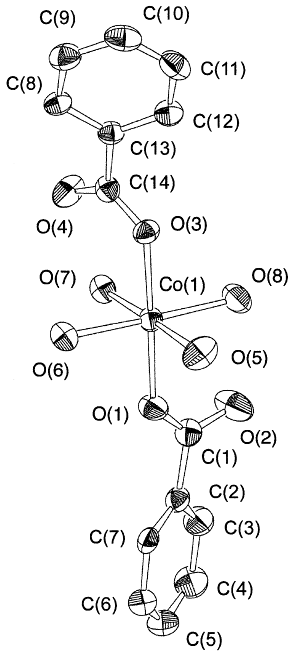


Fig. 1. Structure of **1** with atomic numbering scheme. Hydrogen atoms are omitted for clarity. Atoms are represented by thermal ellipsoids at the 50% probability level. Same numbering is adopted for **2**.

Table 2. Selected Bond Distances (Å) and Angles (°) in **1** and **2**

Co(1)–O(1)	2.042(2)	Co(1)–O(3)	2.063(2)
Co(1)–O(5)	2.168(3)	Co(1)–O(6)	2.096(2)
Co(1)–O(7)	2.115(2)	Co(1)–O(8)	2.097(2)
O(1)–Co(1)–O(3)	176.98(8)	O(1)–Co(1)–O(5)	88.0(1)
O(1)–Co(1)–O(6)	90.14(9)	O(1)–Co(1)–O(7)	90.26(9)
O(1)–Co(1)–O(8)	91.71(9)	O(3)–Co(1)–O(5)	90.20(9)
O(3)–Co(1)–O(6)	87.56(9)	O(3)–Co(1)–O(7)	91.59(8)
O(3)–Co(1)–O(8)	90.62(9)	O(5)–Co(1)–O(6)	92.6(1)
O(5)–Co(1)–O(7)	178.2(1)	O(5)–Co(1)–O(8)	88.4(1)
O(6)–Co(1)–O(7)	87.36(8)	O(6)–Co(1)–O(8)	177.9(1)
O(7)–Co(1)–O(8)	91.7(1)		
Ni(1)–O(1)	2.021(2)	Ni(1)–O(3)	2.037(2)
Ni(1)–O(5)	2.111(3)	Ni(1)–O(6)	2.071(2)
Ni(1)–O(7)	2.065(2)	Ni(1)–O(8)	2.055(3)
O(1)–Ni(1)–O(3)	176.09(9)	O(1)–Ni(1)–O(5)	87.0(1)
O(1)–Ni(1)–O(6)	89.23(9)	O(1)–Ni(1)–O(7)	90.35(9)
O(1)–Ni(1)–O(8)	93.0(1)	O(3)–Ni(1)–O(5)	90.31(9)
O(3)–Ni(1)–O(6)	88.03(9)	O(3)–Ni(1)–O(7)	92.30(9)
O(3)–Ni(1)–O(8)	89.7(1)	O(5)–Ni(1)–O(6)	92.5(1)
O(5)–Ni(1)–O(7)	177.4(1)	O(5)–Ni(1)–O(8)	88.6(1)
O(6)–Ni(1)–O(7)	87.13(9)	O(6)–Ni(1)–O(8)	177.5(1)
O(7)–Ni(1)–O(8)	91.8(1)		

The metal centers adopt a distorted octahedral geometry with a pseudo square-planar $M(H_2O)_4$ and two carboxylate oxygen atoms at the *trans*-positions. The M–OH_2 distances lie in the range of 2.096(2)–2.168(3) Å and have angles of 91.7(1)–92.6(1)°. The M–O(carboxylate) distances are 2.042(2) and 2.063(2) Å. The latter suggests a slightly compressed octahedron. The O–Co–O angle is 177°. The Co···Co distance within a chain is 4.990 Å with M–OC_6O–M connectivity; and the next nearest Co–Co is 7.5 Å. The latter defines the pitch of the helix and corresponds to two formula units. The nearest

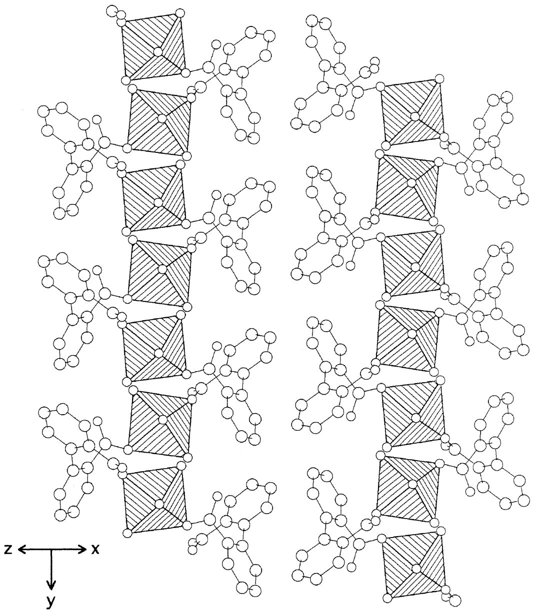


Fig. 2. Helical structure of two adjacent chains in **1** running clockwise (left) and anticlockwise (right).

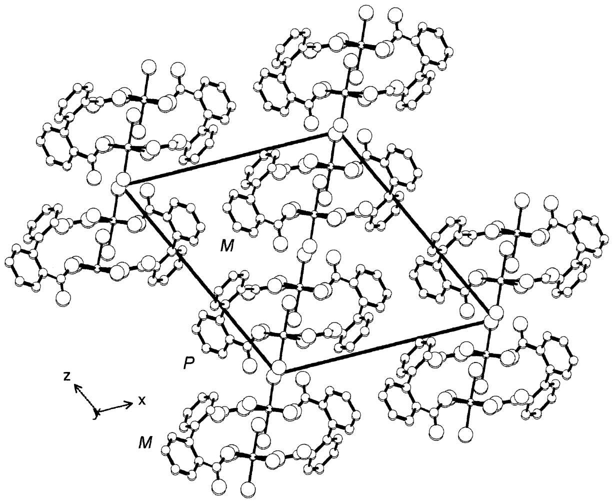


Fig. 3. Packing of the helices in **1** viewed down the chain.

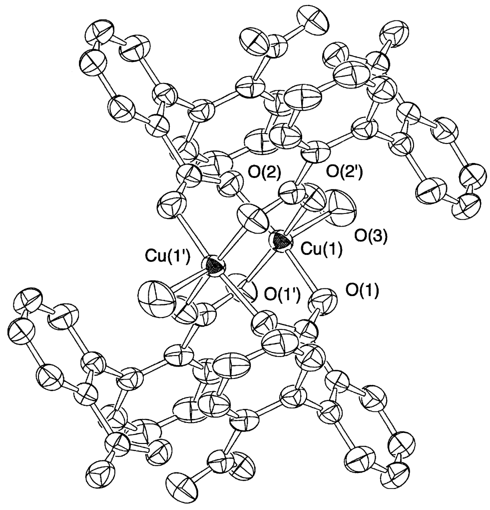


Fig. 4. Structure of a ladder in **3**. Hydrogen atoms are omitted for clarity. Atoms are represented by thermal ellipsoids at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (°) in **3**

Cu(1)–O(1)	1.949(4)	Cu(1)–O(1′)	1.949(4)
Cu(1)–O(2)	1.952(4)	Cu(1)–O(2′)	1.952(4)
Cu(1)–O(3)	2.225(6)		
O(1)–Cu(1)–O(1)	88.6(3)	O(1)–Cu(1)–O(2)	169.8(2)
O(1)–Cu(1)–O(2′)	90.6(2)	O(1)–Cu(1)–O(3)	99.2(2)
O(1)–Cu(1)–O(3′)	99.2(2)	O(2)–Cu(1)–O(2′)	88.4(2)
O(2)–Cu(1)–O(3)	91.0(2)	O(2)–Cu(1)–O(3′)	91.0(2)

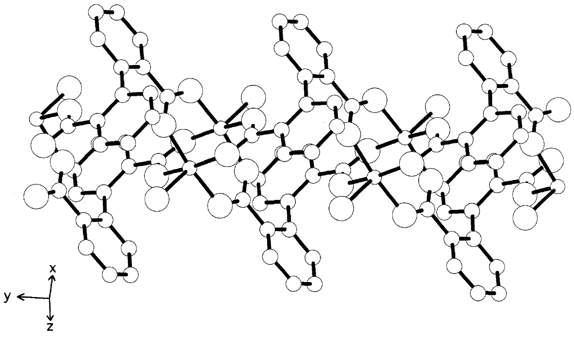


Fig. 5. Structure of a single ladder of **3**. The water molecules and the hydrogen atoms are omitted for clarity.

Co···Co distances between adjacent chains are 5.746, 6.404 and 8.032 Å; those between layers are 12.66–14.45 Å.

This particular structure contains an equal number of *M*- and *P*-helices (Figs. 2 and 3). Therefore, no optical activity is expected. The helices are parallel to the *y*-axis, and alternate within the *xz*-plane. The helices are knitted together by several hydrogen bonds between the oxygen atoms of the carboxylates and the hydrogen atoms of the coordinated water molecules. Several hydrogen bonds are found not only within the chains, but also between the chains. The interchain bond distance between O(7) and O(2) is 2.638(2) Å. The intrachain bond is found between a coordinated water molecule and uncoordinated carboxylate oxygen atoms (O(8)–O(2), 2.604 Å).

These hydrogen bonds create a 2D-network with all the metals aligned in planes separated by the phenyl groups. The two carboxylate groups are both coordinated to the same layer, in contrast to the layered structure of Co(H_2O)$_2$(terephthalate), which is composed of layers of octahedral CoO_6 bridged by the terephthalate dianion.[26]

Structure of 3. The structure of **3** consists of a Cu(II), DPhA ligand and a water molecule. Figure 4 shows an ORTEP drawing of the dimer motif of **3** with the atomic-numbering scheme. Selected bond distances and angles with their estimated standard deviations are listed in Table 3. The repeating structural motif is a propeller dicopper-tetracarboxylate dimer (Fig. 5). The structure is composed of one-dimensional chains of these dimers, parallel to the *b*-axis (Fig. 6). Because the copper atoms within a dimer are symmetry related, all copper atoms in the chain are equivalent. Each copper atom has

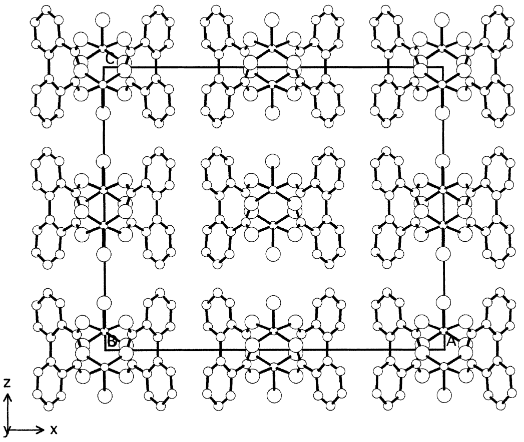


Fig. 6. Packing of the ladders in **3** viewed along the *b*-axis.

two short Cu–O bonds (1.949(4) and 1.952(4) Å) with the DPhA ligands and one long with the oxygen atom of the water molecule (2.225(6) Å). The Cu···Cu distance within the dimer is 2.58 Å, which lies within the range found in previously reported dicopper-tetracarboxylate dimers. The Cu···Cu distances in the coper carboxylate dimers span the narrow range of 2.57 – 2.63 Å, and no dependence of the length on the substituent R of the carboxylate ligand has been found.[42]

The geometry of the dianion in the present compounds is similar to those found in the pure acid and in **1** and **2**. The two phenyl rings are arranged in a near-orthogonal geometry. The carboxylate groups are slightly out of the plane of the phenyl rings. The dihedral angle between the CO_2 groups and the C_6 ring is about 14°, which is smaller than that of **1**. The copper dimers are bridged by both the *P* and *M* forms of the ligand. Thus, two enantiomers are present within the same chain, in contrast to segregation of *P* and *M* forms in different chains for **1** and **2**. Another point of difference is the hydrogen-bonding interactions. The coordinated water molecules act as hydrogen donors to generate a two-dimensional layer structure in **1** and **2**; however, the water molecules of **3** show no hydrogen-bonding interactions between the ladders. One of the possible reasons is the coordination mode of the DPhA ligand. The DPhA ligand acts as a monodentate ligand to bind a metal ion, and the other oxygen atom of the acid becomes the hydrogen acceptor site in **1** and **2**. Because the DPhA ligand acts as a bidentate ligand to bridge two metal centers in **3**, no more hydrogen bonding sites are provided. The packing of the ladders is not very efficient due to the orientation and bulkiness of the diphenyl groups. Some narrow cavities appear between the ladders that may be appropriate for gas sorption.[43]

Thermogravimetry. The thermal analysis of **1** and **2** and the associated heat flow are shown in Fig. 7. Both compounds are stable up to 85 °C. They lose a total of four molecules of water endo-thermically upon heating up to 165 °C. There is a difference of 25 °C between the cobalt and nickel complexes, suggesting a slightly stronger M–OH_2 bond for **2**. The second step is the exothermic decomposition of the organic moiety, which spans 280–350 °C. The resulting products are the expected oxides, Co_3O_4 and NiO.

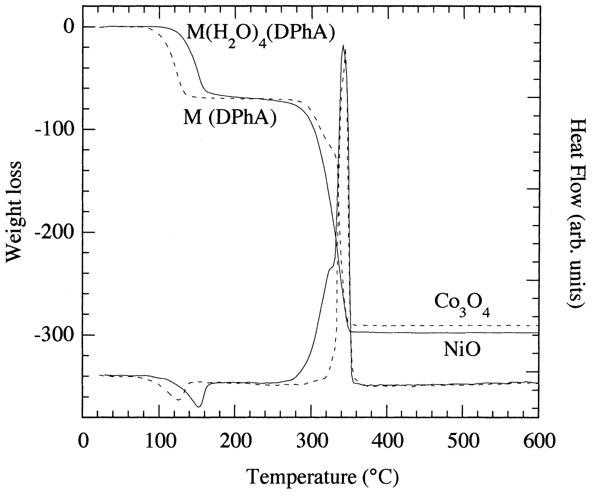


Fig. 7. Thermogravimetry and heat flow for **1** (dashed lines) and **2** (solid lines).

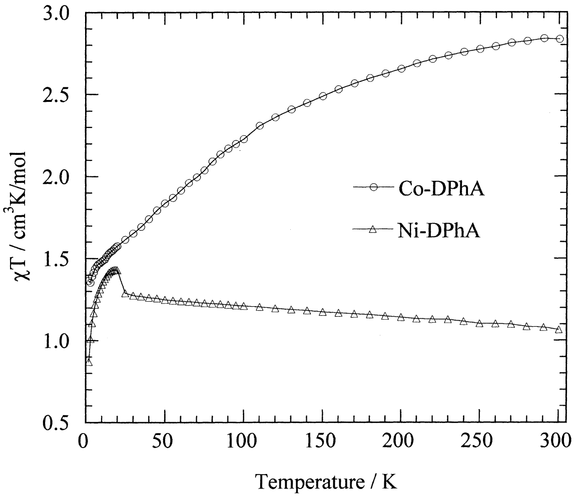


Fig. 8. Temperature dependence of the χT and $1/\chi$ for **1** and **2**.

Magnetic Properties. The magnetic susceptibilities of the three compounds were studied as a function of the temperature in a fixed magnetic field and the isothermal magnetization in a field of up to 5 T at 2 K. The results for **1** and **2** are shown in Figs. 8 and 9. The moment of **1**, presented as the product of the susceptibility and temperature, shows a gradual decrease upon lowering the temperature; the data above 150 K fit the Curie-Weiss function with $C = 3.34(1)$ cm^3 K/mol, $\theta = -51(1)$ K. The calculated moment is $\mu_{eff} = 5.17$ μ_B, which is on a higher side of the expected value for an octahedral coordinated cobalt(II). This may be the effect of a distortion of the octahedron, and the consequent, dark-red coloration. The negative Weiss temperature suggests an antiferromagnetic exchange between near neighbors. However, the Weiss temperature derived from the fit also reflects the effect of spin-orbit coupling, which is of the order of -20 K in the case of a free ion assuming a spin orbit coupling of 170 cm^{-1}.[44] A similar analysis for **2** gives $C = 0.985(9)$ cm^3 K/mol and $\theta = +27(2)$ K. The effective moment ($\mu_{eff} = 2.81$ μ_B) is as expected for octahedral Ni(II). The positive Weiss temperature suggests a considerable ferromagnetic exchange. However, at low tem-

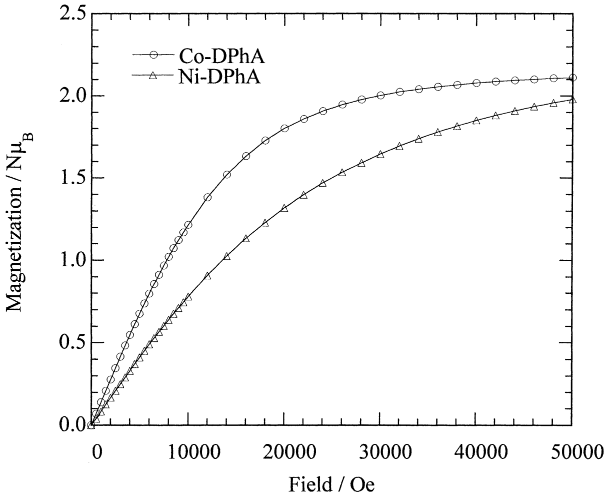


Fig. 9. Isothermal magnetization at 2 K for **1** and **2**.

perature the moment decreases rapidly. This may be due to either a short-range antiferromagnetic exchange between helices, or due to the effect of single-ion anisotropy.[16] To thoroughly check the latter, single-crystal measurements are needed. A jump in the χT value at 20 K was observed, and a very small amount of impurity of $Ni(OH)_2$ derivative was assumed. The isothermal magnetization at 2 K for **1** and **2** are shown in Fig. 9. In both cases, the magnetization increases upon increasing the field according to the Brilloiun function. The value at saturation for **1** is consistent with an effective $s = 1/2$ and anisotropic g-values, as also found by the temperature-dependence susceptibility. The moment for **2** is consistent with an $s = 1$ for Ni in octahedral coordination.

The susceptibility of the copper compound is characterized by a broad maximum at 250 K, and its value is almost negligible below 50 K. This behavior is as expected for copper dimers and is consistent with the singlet-triplet model.[45] A fit of the data gives a singlet-triplet gap of 470 ± 10 K. However, due to a strong exchange within the dimmer, and a large separation between dimers, it is very difficult to estimate the expected small exchange energy between the dimers.

Conclusion

In this study we synthesized metallo-helicates (Co and Ni) and ladder (Cu) using 2,2′-biphenyldicarboxylic acid in which it contains two sterically hindered carboxylate groups. An equal number of two optically active chains co-crystallize in the case of cobalt and nickel. For copper, ladders of dimeric units are favored due to the strong stability of the tetracarboxylato-dicopper unit, and each ladder contains the two enantiomers.

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