Synthesis, Crystal Structure and Magnetic Properties of the Helical-Chain Compounds $[M_2(O_2CC_{12}H_8CO_2)_2(H_2O)_8]$ [M = Cobalt(II), Nickel(II)]

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New 1D complexes are obtained from the reaction of 1,1′-biphenyl-2,2′-dicarboxylic acid (diphenic acid) with KOH and $[Co(NO_3)_2{\cdot}6H_2O]$ or $[Ni(NO_3)_2{\cdot}6H_2O]$ under hydrothermal conditions. Compounds **1** and **2** are isostructural and their structure consists of stacked helical chains of octahedral metal(II) ions. Magnetic measurements show that the Co^{II} atoms in compound **1** are quasi-isolated. In compound **2**, the Ni^{II} chains exhibit a ferromagnetic behaviour. From a simple model derived from the scaling theory of phase transition, the exchange coupling between neighbouring Ni^{II} atoms is evaluated at $J = +1.06$ K. A zero-field splitting effect is observed below 16 K.

Introduction

Low-dimensional magnetism (1D, 2D) is an important research field for chemists interested in the design of new magnetic materials and a better understanding of the mechanisms responsible for their magnetic behaviours.[1−4] Correlations between the magnetic properties of molecule-based solids and their structure or the nature of the chemical bond is largely used for the design of new materials, including high T_C magnets.[5−8] In this context, helicate structures are of current interest in supramolecular coordination chemistry, mainly for their similarity with the structure of the DNA molecule.[9−11] Very few of these studies discuss the effect of the helical arrangement of spin carriers on the magnetic properties[12−14] even though chirality is known to induce photo-magnetic effects.[15] For the design of new coordination compounds with extended structures, the solvo- or hydrothermal route is currently being developed by several research teams involved in solid-state coordination chemistry,[16,17] and organic-inorganic materials,[18−20] including helical chain compounds[21,22] and mesoporous (possibly magnetic) materials.[23−25] In this approach, the organic ligand acts as a template, the structure of the product being closely related to the geometry and the number of coordination sites provided by the ligand. Important results have recently been obtained in the field of low dimensional magnetic materials exhibiting unusual behaviours.[26−29]

The present paper describes the crystal structure and the magnetic properties of new Ni^{II} and Co^{II} coordination polymers synthesised by using self-assembly in hydrothermal conditions and exhibiting helical chains based on an inexpensive ligand, the 1,1′-biphenyl-2,2′-dicarboxylate.

Results and Discussion

Compounds **1** and **2** were synthesised by the hydrothermal method from cobalt(II) nitrate, and nickel(II) nitrate, respectively, with diphenic acid, potassium hydroxide and water in a 2:3:8:120 ratio, at 170 °C during 72 h (see Exp. Sect.). The title compounds are obtained in good yields, and crystallise as large (mm size), thin platelets. In the case of compound **1**, another phase is also observed as purple needle-shaped crystals, whose structure and properties will be reported elsewhere. The synthetic conditions can be optimised in order to favour compound **1**, and pure compound **1** is easily obtained by manual separation of the largest crystals. The formula of both compounds **1** and **2** has been checked by chemical analysis, and ancillary characterisation techniques, and their structure has been determined by single crystal X-ray diffraction at room and low temperature (see Exp. Sect.). The principal distances are reported in Table 1.

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Table 1. Selected bond lengths (Å) and angles (°); symmetry codes: (i) 1/2 − *x*, 1/2 + *y*, 1/2 − *z*, (ii) −*x*, 2 − *y*, −*z*, (iii) *x* − 1, *y* + 1, *z*, (iv) *x* − 1/2, 3/2 − *y*, *z* + 1/2

Compound **1**			
Co−O1	2.0989(13)	Co−O4	2.1216(13)
Co−O2	2.1727(16)	Co−O5	2.0462(12)
Co−O3	2.1066(14)	Co−O6	2.0632(11)
O8...O3(H14)	2.618(2)	O8^{ii}...O4(H8)	2.645(1)
O8···H14	1.90(3)	O8^{ii}···H8	1.83(2)
O7...O4(H15)	2.612(2)	O6^{i}...O1(H6)	2.705(2)
O7···H15	1.83(3)	O6^{i}···H6	1.96(2)
C6^{iv}...C11	3.734(4)	C4^{iii}...C13	3.875(4)
O1−Co−O3	177.60(6)	O1−Co−O6	87.73(5)
O1−Co−O2	92.58(6)	O5−Co−O6	177.07(5)
O1−Co−O4	87.36(5)	O2−Co−O4	178.42(7)
O1−Co−O5	90.12(5)		
O8···H14−O3	160(3)	O8^{ii}···H8−O4	174(2)
O7···H15−O4	160(3)	O6^{i}···H6−O1	162(2)
Compound **2**			
Ni−O1	2.0713(11)	Ni−O4	2.0652(11)
Ni−O2	2.1105(12)	Ni−O5	2.0257(10)
Ni−O3	2.0641(13)	Ni−O6	2.0407(10)
O8...O3(H14)	2.598(2)	O8^{ii}...O4(H8)	2.635(2)
O8···H14	1.82(3)	O8^{ii}···H8	1.81(2)
O7...O4(H15)	2.592(2)	O6^{i}...O1(H6)	2.684(2)
O7···H15	1.74(3)	O6^{i}···H6	1.94(2)
C6^{iv}...C11	3.689(3)	C4^{iii}...C13	3.839(4)
O1−Ni−O3	176.68(5)	O1−Ni−O6	87.86(4)
O1−Ni−O2	92.58(5)	O5−Ni−O6	176.41(4)
O1−Ni−O4	86.89(4)	O2−Ni−O4	177.61(5)
O1−Ni−O5	89.41(4)		
O8···H14−O3	160(3)	O8^{ii}···H8−O4	170(2)
O7···H15−O4	162(2)	O6^{i}···H6−O1	161(2)

Compounds **1** and **2** are isostructural. The crystal cell parameters of **2** are slightly smaller than for **1**[30] in agreement with the smaller metal−oxygen bond lengths for the nickel(II) ions compared to cobalt(II) as also found in aqua complexes and η^1-carboxylates.[31] The molecular structure consists of divalent metal atoms, located in slightly distorted octahedral sites (Figure 1 and Table 1). Water molecules (O1 to O4) are located at the four basal positions [mean Co−O = 2.1249(14) Å, mean Ni−O = 2.0778(13) Å] whereas the apical ones [mean Co−O = 2.0547(12) Å, mean Ni−O = 2.0332(10) Å] are occupied by oxygen atoms of carboxylate groups (O5 and O6). Only one oxygen of each carboxylate group is coordinated to a metal atom, the other one being involved in short hydrogen bonds with hydrogen atoms of the neighbouring water molecules [O8···O3(H14), O8^{ii}···O4(H8), in Table 1 (A in Figure 2), and O7···O4(H15) (B in Figure 3)]. The M^{2+} ions form helical chains running along the *b* axis (Figure 3). These ions

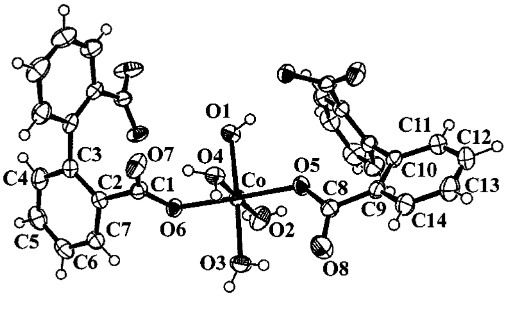

Figure 1. Molecular structure and atomic labels (asymmetric unit only) of the non-H atoms for compound **1**; both biphenyldicarboxylate ligands have been completed using the 1/2 − *x*, *y* − 1/2, 1/2 − *z* symmetry element; compound **2** exhibits the same structure, with Ni instead of Co

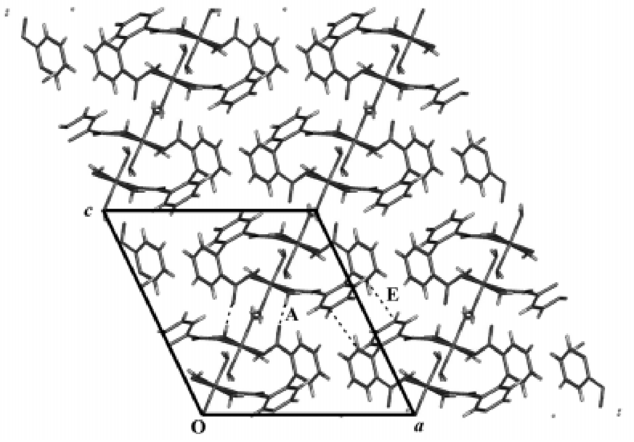

Figure 2. Perspective view of the molecular packing along the *b* axis, showing the helical stacking (H atoms omitted for clarity); inter-chain hydrogen bonds between O8^{ii} and H8 [O8^{ii}···O4(H8)] are drawn as dashed lines (label A); inter-chain short C6^{iv}···C11 interactions are drawn as dashed lines (label E); symmetry codes given in Table 1

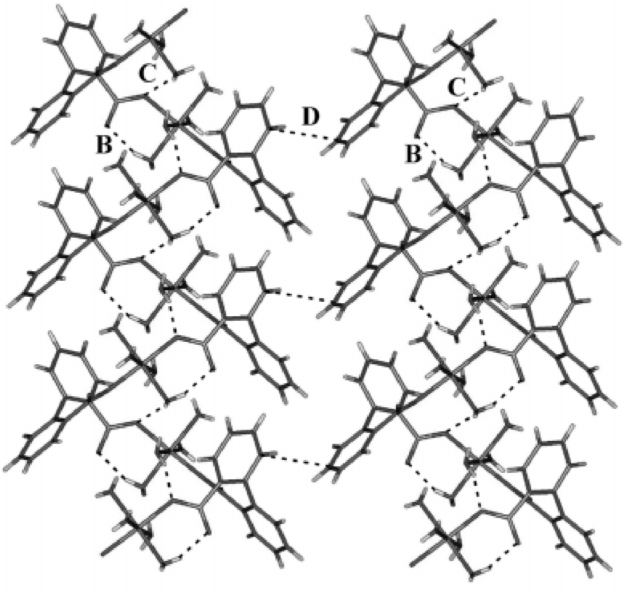

Figure 3. View of two neighbouring M^{II} helical chains; in one chain, the shortest M−M distance is 4.9981(3) Å for M = Co, and 4.9373(3) Å for M = Ni; intra-chain short hydrogen bonds between O7 and H15 [O7···O4(H15)] and between O6^{i} and H6 [O6^{i}···O1(H6)] are drawn as dashed lines (B and C respectively); inter-chain short C4^{iii}···C13 contacts are drawn as dashed lines (D); symmetry codes given in Table 1

are connected through the biphenyldicarboxylate ligand, the shortest M···M distance along the chain being 4.9981(3) Å and 4.9373(3) Å, for Co and Ni, respectively. The shortest exchange pathway involves a short intra-chain hydrogen bond (C in Figure 3) between O6^i and H6 [O6^i···O1(H6) = 2.705(2) Å in **1** and O6^i···O1(H6) = 2.684(2) Å in **2**]. The two aromatic rings of each ligand are tilted around the C3−C10 bond by 85.96(8)° and 87.2(1)° for **1** and **2**, respectively. Moreover, the chains are connected by inter-chain hydrogen bonds (A in Figure 2) to form planes quasi perpendicular to the [1 0 $\bar{1}$] direction. The metal atoms are arranged in a zigzag manner between the planes. Phenyl-phenyl contacts in a T-shape arrangement (cf. D,E in Figure 2 and 3, and C6^{iv}···C11, C4^{iii}···C13 distances in Table 1) ensure inter-plane connections. In E contacts, the corresponding aromatic rings stack almost perpendicular to each other, the dihedral angle between the best planes corresponding to the two rings is 86.10(6)° for **1** and 85.46(6)° for **2**. Contacts D involve similar inter-plane contacts, the corresponding dihedral angles being 115.47(6)° and 113.82(4)° for **1** and **2**, respectively. In each of these inter-plane contacts, the positively charged C−H groups of one aromatic ring probably interact with the negatively charged π-electron cloud of the other aromatic ring.[32] No parallel π−π stacking of the phenyl rings results from the present geometrical configuration.

The IR spectra of both compounds exhibit the same features, as would be expected from their structural homology. The frequency difference between the symmetric and antisymmetric carboxylate vibrations, $\Delta\nu$ = 141 cm^{-1}, is small but in agreement with the unidentate coordination mode of the carboxylate groups;[33] this small value can be explained by the occurrence of hydrogen bond involving the oxygen atom that is not linked to the metal atom, thus giving a bidentate character to the carboxylate groups. The presence of two broad ν(O−H) bands in the range 3200−3400 cm^{-1} is due to the two hydrogen-bonded *aqua* ligands. As for the UV spectra shown in Figure 4, it corroborates the octahedral geometry of Co^{II} and Ni^{II} ions.[34,35] The values of *Dq* (1050 cm^{-1} for **1** and 877 cm^{-1} for **2**) and Racah's parameter *B* (862 cm^{-1} for **1** and 1005 cm^{-1} for **2**), deduced from the transitions observed, agree with a low crystal field (*Dq*/*B* = 1.2 for **1** and *Dq*/*B* = 0.9 for **2**) and an octahedral high-spin configuration for the metal centres, which can also be inferred from the magnetic findings (see below).

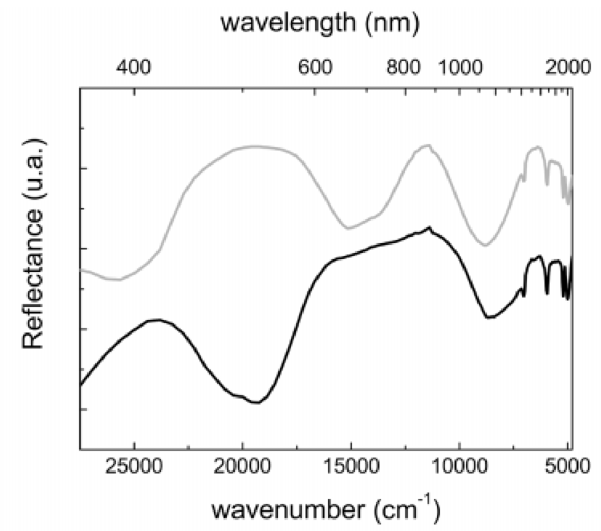

Figure 4. UV spectra of compounds **1** (below) and **2** (upper curve)

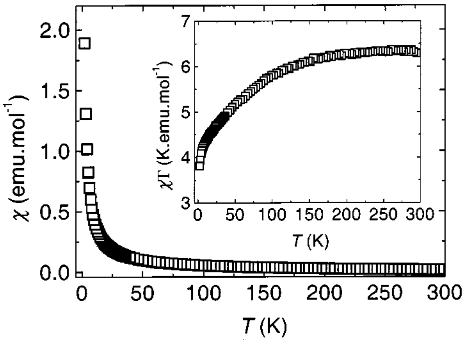

Figure 5. Magnetic susceptibility and χT product of compound **1**

The magnetic properties of **1** and **2** were investigated as described in the Exp. Sect.. The temperature variation of the magnetic susceptibilities χ of **1** is shown in Figure 5, after correction for diamagnetic contributions. Upon cooling down, $\chi = f(T)$ increases continuously up to a maximum of 1.9 emu·mol^{-1} at 2 K. The χT product exhibits a regular decrease from 6.36 emu·K·mol^{-1} at 300 K to 3.81 emu·K·mol^{-1} at 2 K. The inverse susceptibility varies linearly with the temperature in the high temperature regime (T > 180 K) and is well fitted in this region by using the Curie−Weiss law, giving C = 6.55 emu·K·mol^{-1} and θ = −8.63 K. The calculated effective moment per metal ion, $\mu_{eff} = (8 \times 1/2 \times C)^{1/2}$ = 5.12 μ_B/Co, agrees with that expected for octahedral high spin Co^{II} ions.[36,37] In accordance with this, the magnetisation vs. field curve at 2 K is characteristic of a paramagnetic phase, with a saturation moment per cobalt(II) ion of Ms = 2.5 $\mu_B$mol^{-1} (expected, 2−3 μ_B per cobalt ion).[36,37]

The decrease of the χT product together with the negative value of θ are well explained by the effect of the spin-orbit coupling for isolated Co^{II} ions in an octahedral crystal field, which results in the splitting of the energy levels arising from the $^4T_{1g}$ ground term, stabilising the $J = \pm 1/2$ doublet that is well separated from the excited states.[36] An antiferromagnetic coupling could also contribute, although this is expected to be very small since the value measured at 2 K (1.9 emu·K per Co^{II} mol) is close to that expected for isolated metal ions in an O$_h$ crystal field (≈1.8 emu·K per Co^{II}).[36] An analytical expression of the susceptibility for isolated Co^{II} ions is reported in the literature,[36] but corresponds to the particular case of a cubic crystal field and it is stated that the magnetic behaviour of such an ion is highly sensitive to site distortion and crystal field variations. Attempts to use this expression for the present compound give not particularly satisfactory results. Likewise no expression is available for Co^{II} chains taking into account the spin-orbit coupling. Thus the fitting of the experimental data to an appropriate model is rather complex for compound **1**, although its behaviour is qualitatively very well explained on the basis of quasi-isolated magnetic centres.

The magnetic behaviour of compound **2** is presented in Figure 6. The $1/\chi = f(T)$ curve fits well the Curie−Weiss law at high temperature ($T > 100$ K) with $C = 2.289$ emu·K·mol^{-1}, in agreement with the value expected for isolated Ni^{II} ions in an octahedral ligand field (giving $\mu_{eff} = 3.03\ \mu_B$/Ni), and $\theta = +1.08$ K, pointing to weak ferromagnetic interactions. Accordingly, the χT product is almost constant from ambient temperature down to about 150 K at a value of approximately 2.3 emu·K·mol^{-1}. Below 150 K, a slight increase up to a maximum of 2.49 emu·K·mol^{-1} at 16 K and a drop down to 1.69 emu·K·mol^{-1} at 2 K are observed. Zero-field splitting is known to occur for nickel(II) ions, and for isolated ions may induce either an increase or a decrease of χT, at very low temperature, depending on the site distortion.[4] It cannot give rise to both at the same time however. The observed behaviour is thus characteristic of the occurrence of ferromagnetic interactions within the chains. The drop to zero below 16 K can be related to antiferromagnetic coupling between the chains together with the effect of zero-field splitting. The absence of any maximum in the χ vs. T curve is rather in favour of the latter mechanism. Moreover, the magnetisation versus field measurement exhibits a paramagnetic-like behaviour. As expected for divalent metal ions, the saturation magnetisation at 2 K is 2 μ_B per nickel, and neither metamagnetic nor spin-flop transitions are observed, suggesting that no 3D antiferromagnetic order is reached at this temperature.

In order to evaluate the exchange interaction between neighbouring nickel(II) atoms, the susceptibility measurements were fitted in the high temperature region by using a simple model for Heisenberg $S = 1$ ferromagnetic regular chains. In this approach, the zero-field splitting for nickel(II) is not taken into account, assuming that its effect is significant only at low temperatures ($T < 16$ K).[38]

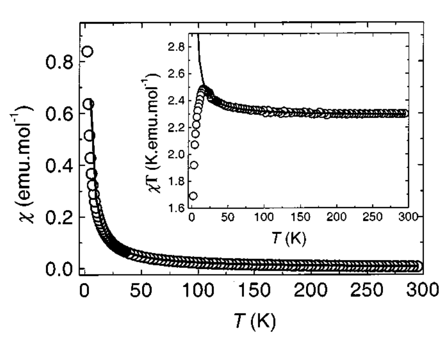

Figure 6. Magnetic susceptibility and χT product of compound **2**; the full line corresponds to the best fit to the expression calculated for a ferromagnetic Heisenberg chain of $S = 1$ spins

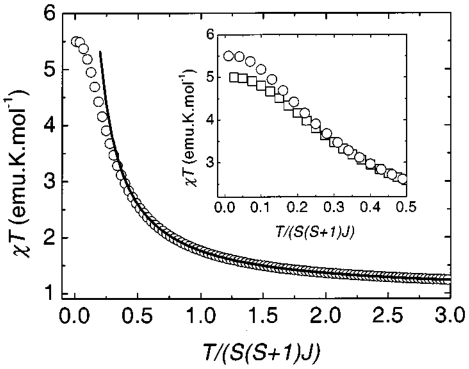

Figure 7. Variation of the χT product as a function of reduced temperature for a Heisenberg chain of 10 (square) and 9 (circle) $S = 1$ spins; the full line corresponds to the best fit of the $N = 10$ system to the power law expression given in the text; the inset is a zoom at low temperature showing the discrepancy between $N = 9$ and $N = 10$ spin chains

The spin-exchange Hamiltonian of the system [Equation (1)] can be solved numerically only for ring chains involving a limited number of spins N. The study of the variation of the susceptibility as a function of the reduced temperature $T_r = T/[S(S + 1)J]$, for chains of various size (up to $N = 10$) shows that data corresponding to N and $N + 1$ chains coincide in a wide range down to a limiting value at low temperatures (inset in Figure 7). This value decreases when N increases and corresponds to the temperature limit above which the calculation for N spins is the exact solution for the infinite chain. Moreover, following the approach developed within the frame of the scaling theory by Souletie,[39,40] the χT product for a regular ferromagnetic $S = 1$ chain can be described in the high temperature range by the power law[41] shown in Equation (2):

$$\hat{H}_{ex} = -J\sum_{i=1}^{N}\hat{S}_i\hat{S}_{i+1} - g\mu_B\sum_{i=1}^{N}\hat{S}_i\vec{H} \qquad (1)$$

$$\chi T = C(1 - T_c/T_r)^{-\gamma} \qquad (2)$$

where C is the Curie constant $[g^2\mu_B^2 S(S + 1)/3k]$, T_c the reduced critical temperature and γ is a critical exponent. With this relation, the $\chi T = f(T_r)$ data for $N = 10$ have been fitted from high temperatures down to the limit ($T_r \approx 0.6$) where it does not coincide with the $N = 9$ calculation (Figure 7) giving the general relation for $S = 1$ Heisenberg ferromagnetic chains shown in Equation (3):

$$\chi T = (g^2\mu_B^2 S(S + 1)/3k)(1 - 0.59679/T_r)^{-1.2322} \qquad (3)$$

Finally, this simple expression fits very well with the experimental susceptibility of compound **2** (Figure 6), giving $g = 2.13$, and $J = +1.06$ K, which is weak and in agreement with the value of θ deduced above.

The crystal structure of the present compounds indicates that the exchange pathways between neighbouring magnetic centres involve the biphenyldicarboxylate ligands and hydrogen bonds. Both are known to promote weak exchange interactions. Indeed, the binuclear 1,1′-biphenyl-2,2′-dicarboxylate transition metal complexes reported in the literature[42] exhibit a quasi-paramagnetic behaviour, and the coupling through hydrogen bonds in molecular materials is likewise very weak.[43] The low efficiency of these exchange pathways explains this behaviour of **1** and also the weak ferromagnetic behaviour observed for **2**, although the magnetic centres are relatively close to each other.

Conclusion

New one-dimensional cobalt(II) and nickel(II) compounds have been synthesised as large single crystals by hydrothermal methods. Their structures have been solved and consist of stacked helical chains, which are generated by using the simple 1,1′-biphenyl-2,2′-dicarboxylate ligand as an efficient template. From the magnetic point of view this ligand appears to be fairly poor for magnetic exchange coupling, as shown by the results obtained for compound **1** where the cobalt(II) ions are quasi-isolated. Nevertheless, in the isostructural compound **2**, the nickel(II) ions are coupled and form ferromagnetic $S = 1$ chains. The present compounds are not chiral since both right hand and left hand orientations of the helical chain are present in the structure. Further work is in progress on related systems in order to isolate enantiomerically pure forms. The purple phase obtained as needle crystals with the compound **1** is currently under investigation.

Experimental Section

General Remarks: Thermogravimetric experiments were performed using a Setaram TG92 instrument (heating rate of 2 °C/min, air stream). FT-IR studies were performed with an ATI Mattson Genesis computer-driven instrument (0.1 mm thick powder samples in KBr). UV/Vis-NIR studies were performed with a Perkin−Elmer Lambda 19 instrument (spectra recorded by reflection with a resolution of 4 nm and a sampling rate of 480 nm/min). Magnetic studies were carried out using a (Quantum Design XMPMS) SQUID magnetometer. Susceptibilities were measured at H = 2000 Oe, in the field range of the linear variation of magnetization versus H.

Bis{cobalt(II)-tetraaqua-biphenyl-2,2′-η^1,η^1-dicarboxylate} (1): $C_{28}H_{32}Co_2O_{16}$ (**1**) was synthesised by the hydrothermal method from $[Co(NO_3)_2{\cdot}6H_2O]$ (98% Aldrich), diphenic acid (1,1′-Biphenyl-2,2′-dicarboxylic acid, 98% Acros), and KOH (85%, SDS). The starting mixture corresponding to the molar composition 2:3:8:120 of $[Co(NO_3)_2{\cdot}6H_2O]$, $C_{14}H_{10}O_4$, KOH and H_2O was homogenised and transferred (170 °C, 72 h, autogenous pressure) to a sealed hydrothermal bomb (23 cm^3 bomb volume) walled with a Teflon liner. Pink plates were obtained, washed and rinsed with deionised water (18.2 MΩcm) and absolute ethyl alcohol (Carlo Erba) (yield > 60% on the basis of $[Co(NO_3)_2{\cdot}6H_2O]$). The purity was confirmed by elemental analysis (EA) {$C_{28}H_{32}Co_2O_{16}$ (742.4): calcd. C 44.6, H 7.5; found C 44.3, H 7.5}, oxidising pyrolysis (OP) {heating in air from 20 to 700 °C at 2 °C/min, 30 min at 700 °C to transform cobalt into Co_3O_4,[44−45] and cooling to 20 °C at 10 °C/min: calcd. Co 15.88; found 15.64}, and ATG weight loss at 172 °C titration of water {calcd. 19.4; found 19.2 }. IR (KBr pellet): $\tilde{\nu}$ = 3612 cm^{-1} (ν OH), 3440 (ν OH−O), 3197 (ν OH−Co), 1598 (ν C−C), 1576 (ν C−C), 1539 (ν_{as} C=O), 1496 (ν C−C), 1440 (ν C−C), 1398 (ν_s C−O), 1267 (in plane δ_b C−H), 1151 (in plane δ_b C−H), 1108 (in plane δ_b C−H), 1049 (in plane δ_b C−H). UV/Vis (reflectance for octahedral coordination of Co^{II}): λ = 1190 nm ($^4T_{1g} \rightarrow {}^4T_{2g}$), 520 nm ($^4T_{1g} \rightarrow {}^4T_{1g}(P)$].

Bis{nickel(II)-tetraaqua-biphenyl-2,2′-η^1,η^1-dicarboxylate} (2): $C_{28}H_{32}Ni_2O_{16}$ (**2**) was synthesised by the hydrothermal method from $[Ni(NO_3)_2{\cdot}6H_2O]$ (98% Aldrich), diphenic acid (1,1′-Biphenyl-2,2′-dicarboxylic acid, 98% Across), and KOH (85%, SDS). The starting mixture corresponding to the molar composition 2:3:8:120 of $[Ni(NO_3)_2{\cdot}6H_2O]$, $C_{14}H_{10}O_4$, KOH and H_2O was homogenised and transferred (170 °C, 72 h, autogenous pressure) to a sealed hydrothermal bomb (23 cm^3 bomb volume) walled with a Teflon liner. Pale green plate crystals were obtained (yield > 90% on the basis of $[Ni(NO_3)_2{\cdot}6H_2O]$), washed and rinsed with deionised water (18.2 MΩcm) and absolute ethyl alcohol (Carlo Erba). The purity was confirmed by elemental analysis (EA) {$C_{28}H_{32}Ni_2O_{16}$ (742.0): calcd. C 45.33, H 4.35; found C 45.3, H 4.35}, oxidising pyrolysis (OP) {heating in air from 20 to 700 °C at 2 °C/min, 30 min at 700 °C to transform nickel into NiO,[44] and cooling to 20 °C at 10 °C/min: calcd. Ni 15.82; found 16.0}, and ATG titration of water {weight loss (%) at 200 °C: calcd. 19.41; found 19.32}. IR (KBr pellet): $\tilde{\nu}$ = 3608 cm^{-1} (ν OH), 3432 (ν OH−O), 3180 (ν OH−Ni), 1598 (ν C−C), 1575 (ν C−C), 1539 (ν_{as} C=O), 1496 (ν C−C), 1442 (ν C−C), 1398 (ν_s C−O), 1269 (in plane δ_b C−H), 1151 (in plane δ_b C−H), 1109 (in plane δ_b C−H), 1049 (in plane δ_b C−H). UV/Vis (reflectance for octahedral coordination of Ni^{II}): λ = 1140 nm ($^3T_{2g} \rightarrow {}^3A_{2g}$), 720 nm ($^1E_g \rightarrow {}^4A_{2g}$), 653 nm ($^3T_{1g}(F) \rightarrow {}^3A_{2g}$), 391 nm ($^3T_{1g}(P) \rightarrow {}^3A_{2g}$).

X-ray Crystallographic Study: $C_{28}H_{32}Co_2O_{16}$, (**1**), M_r = 742.40, monoclinic, $P2_1/n$ (No. 14), a = 14.3800(4) Å, b = 7.5373(2) Å, c = 15.6142(5) Å, β = 115.3850(10)°, V = 1528.96(8) $Å^3$, Z = 2, D_x = 1.613 g cm^{-3}, μ (Mo-K_α) = 1.155 mm^{-1}, $F(000)$ = 764, T = 293(2) K. A total of 5173 independent reflections (N_{tot} = 36455, R_{int} = 4.70%) were measured on a Nonius Kappa CCD. Absorption corrections were performed by Gaussian integration (ABSORB, DeTitta, 1985[46]) using the crystal shape (T_{min} = 0.688, T_{max} = 0.850), $R[F^2 > 2\sigma(F^2)]$ = 0.056, $wR(F^2)$ = 0.083. The structure was solved by direct methods (SHELXS, Sheldrick 1997[47]) and refined on F^2 by using full-matrix least-squares techniques (SHELXL, Sheldrick 1997[48]). All H atoms were located in the difference Fourier map and refined isotropically, all non-H atoms were refined anisotropically.

$C_{28}H_{32}Ni_2O_{16}$, (**2**), M_r = 741.96, monoclinic, $P2_1/n$ (No. 14), a = 14.3092(4) Å, b = 7.4605(2) Å, c = 15.4260(5) Å, β = 115.4540(10)°, V = 1486.93(8) $Å^3$, Z = 2, D_x = 1.612 g cm^{-3}, μ (Mo-K_α) = 1.345 mm^{-1}, $F(000)$ = 768, T = 110(2) K. A total of 8129 independent reflections (N_{tot} = 48871, R_{int} = 4.80%) were measured on a Nonius Kappa CCD. Absorption corrections were performed by Gaussian integration (ABSORB, DeTitta, 1985) using the crystal shape (T_{min} = 0.701, T_{max} = 0.908), $R[F^2 > 2\sigma(F^2)]$ = 0.042, $wR(F^2)$ = 0.091. The structure was solved by direct methods (SHELXS, Sheldrick 1997[47]) and refined on F^2 using full-matrix least-squares techniques (SHELXL, Sheldrick 1997[48]). All H atoms were located in the difference Fourier map and refined isotropically, all non-H atoms were refined anisotropically.

CCDC-158624 (**1**) and -168731 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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