Syntheses, Structure and Magnetic Properties of the First $\mu_{1,5}$-Dicyanamido-Bridged Dinuclear Compounds $[Ni(\mu_{1,5}\text{-}dca)(dca)(dpt)]_2$ and $[Ni(\mu_{1,5}\text{-}dca)(dca)(medpt)]_2$

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Keywords: N ligands / Bridging ligands / Nickel / Magnetic properties

The first structural determination of dinuclear compounds with $\mu_{1,5}$-dicyanamide [dca, $N(CN)_2^-$] as bridging ligand has been achieved with the products of formula $[Ni(\mu_{1,5}\text{-}dca)(dca)(dpt)]_2$ (**1**) and $[Ni(\mu_{1,5}\text{-}dca)(dca)(medpt)]_2$ (**2**) [dpt = bis(3-aminopropyl)amine and medpt = bis(3-aminopropyl)methylamine]. The X-ray diffraction analysis reveals dinuclear compounds with double $\mu_{1,5}$-dicyanamide bridges. The nickel atoms are hexacoordinate. The small differences in the terminal ligand (dpt or medpt) create a drastic change in the magnetic behaviour: the susceptibility measurements of **1** show weak antiferromagnetic coupling ($J = -1.2$ cm^{-1}, $g = 2.29$) whereas those of **2** show ferromagnetic coupling ($J = 0.7$ cm^{-1}, $g = 2.17$). The related compound (μ-terephthalato)$[Ni(dca)(dpt)(H_2O)]_2$ (**3**) is also described. The X-ray diffraction analysis reveals a dinuclear terephthalato-bridged Ni^{II} compound with terminal dca ligands. The susceptibility measurements of **3** indicate weak antiferromagnetic coupling: $J = -0.3$ cm^{-1}, $g = 2.13$.

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Introduction

The dicyanamide ligand [dca, $N(CN)_2^-$] has been extensively used during the last few years to generate a wide variety of polynuclear compounds of different topologies and magnetic properties: 3-D compounds of general formula $[M(dca)_2]$ which order magnetically as weak ferro- or antiferromagnets[1−5] and low-dimensional systems (2D or 1D) with general formula $[M(L)_x(dca)_2]_n$ showing weak antiferromagnetic coupling have been obtained.[5−14] Another way of synthesising 3D systems with general formula $[M(L)(dca)_2]$ is by using ancillary ligands such as pyrazine, 4,4′-bipyridine, pyrimidine and 2,2′-bipyrimidine in addition to the dicyanamido ligand.[15−21] The $[M(L)(dca)_2]$ (L = pyrazine) compound exhibits long-range magnetic-ordering below 2.53(2) K.[19] Surprisingly, structurally described dinuclear dca compounds are rare: as far as we know, no dinuclear compounds with $\mu_{1,5}$-dicyanamide bridging ligands have been reported to date. Following our work in this field, we report in this paper the synthesis and magnetostructural characterisation of the first dinuclear $\mu_{1,5}$-dca derivatives with formula $[Ni(\mu_{1,5}\text{-}dca)(dca)(dpt)]_2$ (**1**) and $[Ni(\mu_{1,5}\text{-}dca)(dca)(medpt)]_2$ (**2**) with double dca bridges.

Alternating chains can be obtained by using two different bridging ligands. We have used this strategy successfully with azido and oxalate.[22,23] Similar attempts using dca and oxalate were unsuccessful, but in an attempt to obtain a mixed dca-terephthalato Ni^{II} chain the dinuclear compound (μ-terephthalato)$[Ni(dca)(dpt)(H_2O)]_2$ (**3**) was obtained. Here the terephthalato anion acts as a bridging ligand between two nickel atoms, whereas the dca anions act as terminal ligands. Susceptibility measurements indicate weak antiferromagnetic coupling for **1** and **3**, while for **2** weak ferromagnetic coupling is shown. The ferromagnetic coupling in low dimensional polynuclear compounds with $\mu_{1,5}$-dicyanamide bridging ligands is rare: it has been found in the sheet-like polymer of formula $[Cu(\mu_{1,5}\text{-}dca)_2(phen)]_n$ and has been attributed to a case of accidental orthogonality between the magnetic orbitals.[24]

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DOI: 10.1002/ejic.200300033

Results and Discussion

Crystal Structures

[Ni($\mu_{1,5}$-dca)(dca)(dpt)]$_2$ (1)

A labelled ORTEP plot of the structure of [Ni($\mu_{1,5}$-dca)(dca)(dpt)]$_2$ (**1**) is shown in Figure 1. Selected bond lengths and angles are reported in Table 1. The structure of the compound consists of dinuclear units of nickel atoms bridged by means of double end-to-end dicyanamide bridges. Each nickel atom is hexacoordinate, with a coordination polyhedron close to octahedral. Hexacoordination is achieved by means of three N atoms belonging to the dpt ligand in a *mer* disposition, two N atoms from the bridging dicyanamide ligands, and one N atom from the terminal dicyanamide ligand. The Ni−N distances are in the range 2.082(5) −2.217(3) Å. Bond angles related to the dicyanamide bridging ligands are Ni(1)−N(7)−C(9) and Ni(1)−N(9)−C(10) of 157.4(3)° and 155.3(3)°, respectively, with a central C(10)−N(8)−C(9) angle of 117.0(3)°. The intradimer Ni−Ni distance is 7.270(3) Å.

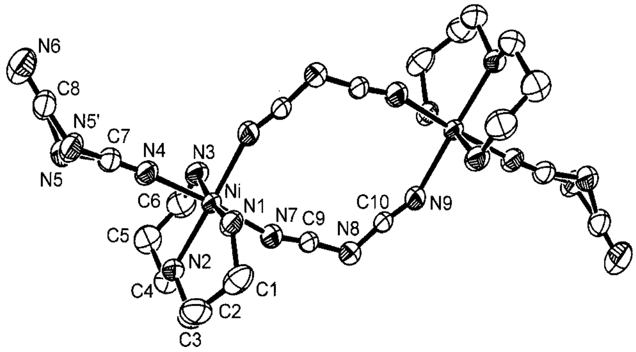

Figure 1. ORTEP drawing of [Ni($\mu_{1,5}$-dca)(dca)(dpt)]$_2$ (**1**)

Table 1. Selected bond lengths (Å) and angles (°) for [Ni($\mu_{1,5}$-dca)(dca)(dpt)]$_2$ (**1**)
Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$

Ni−N(3)	2.082(5)	Ni−N(1)	2.087(4)
Ni−N(4)	2.130(4)	Ni−N(7)	2.146(4)
Ni−N(2)	2.208(3)	Ni−N(9)#1	2.217(3)
N(4)−C(7)	1.149(4)	N(5)−C(7)	1.326(14)
N(5)−C(8)	1.367(16)	N(6)−C(8)	1.160(5)
N(7)−C(9)	1.127(4)	N(8)−C(9)	1.316(5)
N(8)−C(10)	1.343(4)	N(9)−C(10)	1.156(4)
N(9)−Ni#1	2.217(3)	N(3)−Ni−N(1)	171.44(14)
N(3)−Ni−N(4)	90.24(15)	N(1)−Ni−N(4)	88.93(15)
N(3)−Ni−N(7)	87.89(16)	N(1)−Ni−N(7)	93.56(15)
N(4)−Ni−N(7)	175.29(13)	N(3)−Ni−N(2)	85.83(15)
N(1)−Ni−N(2)	102.67(15)	N(4)−Ni−N(2)	88.84(12)
N(7)−Ni−N(2)	86.72(12)	N(3)−Ni−N(9)#1	94.38(15)
N(1)−Ni−N(9)#1	77.09(14)	N(4)−Ni−N(9)#1	89.11(13)
N(7)−Ni−N(9)#1	95.34(13)	N(2)−Ni−N(9)#1	177.94(12)
C(7)−N(5)−C(8)	118.0(10)	C(7)−N(5′)−C(8)	119.4(10)
C(9)−N(7)−Ni	157.4(3)	C(9)−N(8)−C(10)	117.0(3)
C(10)−N(9)−Ni#1	155.3(3)	N(4)−C(7)−N(5′)	164.1(6)
N(4)−C(7)−N(5)	160.8(7)	N(6)−C(8)−N(5′)	161.6(7)
N(6)−C(8)−N(5)	164.5(6)	N(7)−C(9)−N(8)	173.5(4)
N(9)−C(10)−N(8)	172.5(4)		

[Ni($\mu_{1,5}$-dca)(dca)(medpt)]$_2$ (2)

A labelled ORTEP plot of the structure of [Ni($\mu_{1,5}$-dca)(dca)(medpt)]$_2$ (**2**) is shown in Figure 2. Selected bond lengths and angles are reported in Table 2. The crystal structure of complex **2** is similar to **1**: dinuclear units of nickel atoms bridged by means of double end-to-end dicyanamide bridges. The Ni−N distances are in the range 2.071(3)−2.176(3) Å. Bond angles related to the dicyanamide bridging ligands are Ni−N(4)−C(8) and Ni−N(5)−C(9) of 165.1(3)° and 151.2(3)°, respectively, with a central C(8)−N(8)−C(9) angle of 122.2(4)°. The Ni−Ni intradimer distance is 7.520(3) Å. The same Ni−Ni intradimer distance is 0.25 Å shorter in **1** due to a lower central NCN(dicyanamide) angle [117.0(3)°]. For comparative purposes, the intermetallic separation inside the dinuclear unit in **2** is about 0.2 Å longer than the values detected in polymeric networks. In fact, in three topologically different structures the distance between Ni ions bridged by two dca ligands ranges from 7.310 to 7.364 Å, as documented in a layered framework, in a ladder-like 1D polymer,[25] and in a molecular tube-like structure.[26]

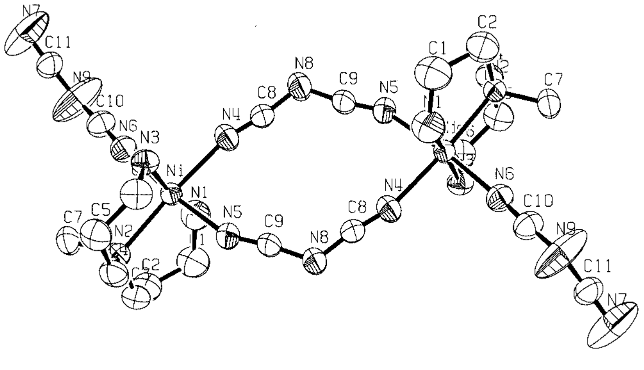

Figure 2. ORTEP drawing of [Ni($\mu_{1,5}$-dca)(dca)(medpt)]$_2$ (**2**)

Table 2. Selected bond lengths (Å) and angles (°) for complex [Ni($\mu_{1,5}$-dca)(dca)(medpt)]$_2$ (**2**)

Ni−N(1)	2.082(4)	Ni−N(4)	2.158(3)
Ni−N(2)	2.176(3)	Ni−N(5)	2.117(3)
Ni−N(3)	2.071(3)	Ni−N(6)	2.092(3)
N(5)−C(9)	1.136(5)	N(8)−C(9)	1.296(6)
N(8)−C(8)	1.297(7)	N(4)−C(8)	1.136(5)
N(1)−Ni−N(2)	94.8(1)	N(3)−Ni−N(4)	87.9(1)
N(1)−Ni−N(3)	172.4(1)	N(3)−Ni−N(5)	94.0(1)
N(1)−Ni−N(4)	87.1(1)	N(3)−Ni−N(6)	88.2(1)
N(1)−Ni−N(5)	91.2(1)	N(4)−Ni−N(5)	84.3(1)
N(1)−Ni−N(6)	86.0(1)	N(4)−Ni−N(6)	89.7(1)
N(2)−Ni−N(3)	90.7(1)	N(5)−Ni−N(6)	173.4(1)
N(2)−Ni−N(4)	174.4(1)	C(8)−N(4)−Ni	165.1(3)
N(2)−Ni−N(5)	90.4(1)	C(9)−N(5)−Ni	151.2(3)
N(2)−Ni−N(6)	95.7(1)	C(10)−N(6)−Ni	176.0(3)
C(8)−N(8)−C(9)	122.2(4)		

(μ-terephthalato)[Ni(dca)(dpt)(H_2O)]$_2$ (3)

A labelled ORTEP plot of the structure of (μ-terephthalato)[Ni(dca)(dpt)(H_2O)]$_2$ is shown in Figure 3. The structure of the compound consists of dinuclear units in which the nickel atoms are bridged by the terephthalato ligand. Each nickel atom is hexacoordinate, with a coordination polyhedron close to octahedral. Hexacoordination is achieved by means of three N atoms belonging to the dpt ligand, one oxygen atom from the monodentate carboxylato ligand, one oxygen atom from the water molecule and, finally, one N atom from the terminal dicyanamido ligand. The bond lengths to the nickel atom are in the range 2.062(7)−2.097(6) Å except the relatively long Ni−O(water) of 2.186(5) Å. The bond angles related to the dicyanamido ligand are in the normal range for this ligand [Ni−N(4)−C(7) = 168.3(10)°], with a central C(7)−N(5)−C(8) angle of 121.4(10)°. The Ni···Ni intradinuclear distance is 11.379(10) Å (Table 3).

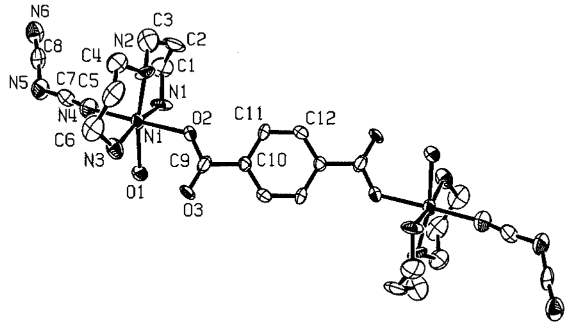

Figure 3. ORTEP drawing of (μ-terephthalato)[Ni(dca)(dpt)(H_2O)]$_2$ (3)

Table 3. Selected bond lengths (Å) and angles (°) for (μ-terephthalato)[Ni(dca)(dpt)(H_2O)]$_2$ (3)
Symmetry transformations used to generate equivalent atoms: #1 $-x-1$, $-y+2$, $-z+1$.

Ni−N(4)	2.062(7)	Ni−N(1)	2.075(7)
Ni−O(2)	2.081(5)	Ni−N(2)	2.083(7)
Ni−N(3)	2.097(6)	Ni−O(1)	2.186(5)
O(2)−C(9)	1.280(8)	O(3)−C(9)	1.215(9)
N(4)−C(7)	1.117(9)	C(7)−N(5)	1.280(9)
N(5)−C(8)	1.292(11)	C(8)−N(6)	1.165(10)
N(4)−Ni−O(2)	174.2(3)	N(1)−Ni−N(3)	169.4(2)
N(2)−Ni−O(1)	169.4(2)	Ni−O(2)−C(9)	130.1(5)
Ni−N(4)−C(7)	168.3(10)	N(4)−C(7)−N(5)	173.3(12)
N(6)−C(8)−N(5)	175.3(10)	C(7)−N(5)−C(8)	121.4(10)

Magnetic Properties

A plot of $\chi_M{\cdot}T$ vs. T for **1** in the temperature range 245−2 K is shown in Figure 4. The overall behaviour of **1** corresponds to an antiferromagnetically coupled system. $\chi_M{\cdot}T$ has a practically constant value of 2.59 cm^3·K·mol^{-1} in the range 245−60 K. In the 60 −2 K range, $\chi_M{\cdot}T$ decreases quickly, reaching 1.19 cm^3·K·mol^{-1} at 2 K. The magnetic data of **1**, in agreement with its dinuclear structure, were analysed by means of an analytical expression based on the Hamiltonian $H = -J\,S_1S_2$ for local spin values $S = 1$. The best fit parameters were $J = -1.2(1)$ cm^{-1} and $g = 2.29(1)$ (Figure 4). Alternatively, the magnetic data of **1** were analysed by considering a non-coupled Ni^{II} mononuclear compound by using an equation[27] that considers only non-interacting $S = 1$ ions in the presence of a single ion anisotropy. The best fit is given by the parameters $D = -10.9(1)$ cm^{-1} and $g = 2.16(1)$. The reliability factors are similar in both cases: 1.5×10^{-4} and 9.8×10^{-4}, respectively. Compound **1** can be considered, according to these data, as a practically non-coupled Ni^{II} compound.

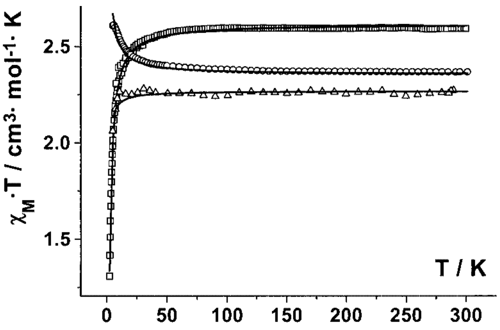

Figure 4. Plot of $\chi_M{\cdot}T$ vs. T for compounds [Ni($\mu_{1,5}$-dca)(dca)(dpt)]$_2$ (**1**) (open squares), [Ni($\mu_{1,5}$-dca)(dca)(Medpt)]$_2$ (**2**) (open circles) and (μ-terephthalato)[Ni(dca)(dpt)(H_2O)]$_2$ (**3**) (open up triangles); the solid line shows the best fit of the data (see text)

A plot of $\chi_M{\cdot}T$ vs. T for **2** in the temperature range 300−5 K is shown in Figure 4. The overall behaviour of **2** corresponds to a ferromagnetically coupled system. $\chi_M{\cdot}T$ has a value of 2.37 cm^3·K·mol^{-1} at room temperature and increases as the temperature decreases, reaching 2.61 cm^3·K·mol^{-1} at 5 K. The increase of the $\chi_M{\cdot}T$ product when T decreases is a clear evidence of a positive J value more important than the ZFS contribution. The magnetic data of **2**, in accordance with its dinuclear structure, were analysed by means of an analytical expression based on the Hamiltonian $H = -J\,S_1S_2$ for local spin values $S = 1$. The best fit parameters were $J = 0.7(1)$ cm^{-1} and $g = 2.17(1)$ (Figure 4). In a previous work[10] we concluded from extended Hückel MO calculations that the dicyanamide $\mu_{1,5}$ bridge possesses two superexchange pathways: t_{2g}-π_y-t_{2g} and e_g-σ-e_g. The t_{2g}-π_y-t_{2g} pathway leads always to weak antiferromagnetically coupled systems, but in cases where this pathway is not active (d^8 and d^9 ions) there exists the possibility of accidental orthogonality via the e_g-σ-e_g pathway for M−*N*−C(dicyanamide) angles around 160°. The positive J value found in **2** is the first experimental evidence of the above proposal in a dinuclear compound.

A plot of $\chi_M{\cdot}T$ vs. T for **3** in the temperature range 300−5 K is shown in Figure 4. The overall behaviour of **3** corresponds to an antiferromagnetically coupled system. $\chi_M{\cdot}$T has a practically constant value of 2.26 cm^3·K·mol^{-1} in the range 300−15 K. In the 15−5 K range, $\chi_M{\cdot}T$ decreases, reaching 2.06 cm^3·K·mol^{-1} at 5 K. The magnetic data of **3**, in accordance with its dinuclear structure, were analysed by means of an analytical expression based on the Hamiltonian $H = -J S_1 S_2$ for local spin values $S = 1$. The best-fit parameters were $J = -0.3(1)$ cm^{-1} and $g = 2.13(1)$ (Figure 4). The very weak J value for **3** is in accordance with the previously published experimental data and MO calculations which conclude that the terephthalate bridge is not a suitable bridging unit to mediate significant exchange coupling.[28]

Experimental Section

[Ni(μ$_{1,5}$-dca)(dca)(dpt)]$_2$ (1): Na[N(CN)$_2$] (13.6 mmol in 30 mL of water), $(C_2H_5)_4NCl\cdot H_2O$ (13.6 mmol in 30 mL of water) and, drop by drop, dpt (6.8 mmol in 10 mL of water) were added successively to a stirred solution of $Ni(NO_3)_2\cdot 6H_2O$ (6.8 mmol in 50 mL of water). Finally a mixture of isophthalic acid (6.8 mmol in 30 mL of water) and NaOH (13.6 mmol in 15 mL of water) was added. The resulting blue solution was left to stand in the air. Blue crystals of **1** suitable for X-ray determination were formed over two weeks. $C_{20}H_{34}N_{18}Ni_2$ (644.0): calcd. C 37.3, H 5.3, N 39.1; found C 37.4, H 5.5, N 39.5.

[Ni(μ$_{1,5}$-dca)(dca)(medpt)]$_2$ (2): Bis(3-aminopropyl)methylamine (Medpt; 1 mmol) was added dropwise to an aqueous solution (10 mL) of $Ni(ClO_4)_2\cdot 6H_2O$ (1 mmol) with constant stirring. A solution of Na[N(CN)$_2$] (2 mmol of) in water (10 mL) was added and a bluish-violet precipitate formed immediately. The reaction mixture was stirred for 30 min and then filtered. After a few days deep bluish-violet single crystals of complex 2 suitable for X-ray diffraction were obtained from the filtrate. $C_{22}H_{38}N_{18}Ni_2$ (672.1): calcd. C 38.28, H 5.66, N 37.49; found C 38.42, H 5.37, N 37.91.

(μ-Terephthalato)[Ni(dca)(dpt)(H$_2$O)]$_2$ (3): Sodium terephthalate (0.723 g, 3.4 mmol in 20 mL of water), Na[N(CN)$_2$] (0.612 g in 20 mL of water), $(C_2H_5)_4NCl\cdot H_2O$ (1.262 g, 6.9 mmol in 20 mL of water) and dpt (0.451 g in 10 mL of water) were added successively to a stirred solution of $Ni(NO_3)_2\cdot 6H_2O$ (1 g, 3.4 mmol) in 30 mL of water. The resulting blue solution was left to stand in the air. Blue crystals of **4** suitable for X-ray determination were formed over ten days. $C_{10}H_{18}N_{10}Ni$ (337.0): calcd. C 34.2, H 5.1, N 23.8; found C 33.9, H 5.3, N 23.7.

Spectral and Magnetic Measurements: Magnetic susceptibility measurements were carried out for **1** and **2** on polycrystalline samples with a SQUID apparatus working in the range 2−300 K for **1** and 5−300 K for **2** in a magnetic field of 0.5 T. Magnetic susceptibility measurements in the temperature range 4−300 K were carried out for **3** on polycrystalline samples with a pendulum-type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat and a Bruker B E15 electromagnet. The magnetic field was approx. 1.5 T. Diamagnetic corrections were estimated from Pascal tables.

Crystal-Structure Determination: The X-ray single-crystal data for **1** and [**3**] were collected on an Enraf−Nonius CAD4 four-circle diffractometer. Crystal size: 0.1 × 0.1 × 0.2 [0.1 × 0.1 × 0.2] mm. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 4. Graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) with the $\omega/2\theta$ technique was used to collect the data sets for **1** and **3**. The accurate unit-cell parameters were determined from automatic centring of 25 reflections, $12 < \theta < 21°$, [25 reflections, $12 < \theta < 21°$] and refined by least-squares methods. 4147 [4740] Reflections were collected in the range $2.67° < \theta < 31.96$ [$2.16° < \theta < 30.15°$]. 1878 [1758] reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Corrections were applied for Lorentz-polarization effects, and for intensity decay during data reduction processing. The structures were solved by direct methods, using the SHELXS[29] computer program, and refined by full-matrix least-squares methods with the SHELXL-97[30] computer program using 4147 [4740] reflections (very negative intensities were not assumed). The function minimised was $\Sigma w| \, |F_o|^2 - |F_c|^2 \,|^2$, where $w = |\sigma^2(I) + (0.0196\ P)^2\,|^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$ for **1** and $w = |\sigma^2(I)|^{-1}$ for **3**. $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from the International Tables of X-ray Crystallography.[31]

For compound **1** sixteen hydrogen atoms were computed and refined, by using a riding model, with an isotropic temperature factor equal to 1.2-times the equivalent temperature factor of the atom to which they are linked. For **3** all H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2-times the equivalent temperature factor of the atom to which are linked. Number of refined parameters: 202 [199]. Maximum and minimum peaks in the final difference synthesis: 0.537 and −0.500 e·Å^{-3} [0.536 and −0.497 e·Å^{-3}]. Significant bond parameters are given in Tables 1 and 3, respectively. For compound **2** data collection was carried at 293(3) K using Mo-K_α radiation (λ = 0.71073 Å) on a Nonius DIP-1030H system (30 frames exposure time of 15 min with a rotation of 6° about , detector being at a distance of 90 mm from the crystal). Crystal size 0.35 × 0.35 × 0.40 mm. Cell refinement, indexing and scaling of the data set were carried out using Mosflm and Scala.[32] 191 Parameters and 4746 reflections, 2880 unique of which 2545 with $I > 2\sigma(I)$. The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[33] All the calculations were performed using the WinGX System, Ver 1.64.[34] Maximum and minimum peaks in the final difference synthesis: 0.543 and −0.511 e·Å^{-3}. Selected bond parameters are given in Table 2.

Table 4. Crystal data and structure refinement for [Ni(μ$_{1,5}$-dca)(dca)(dpt)]$_2$ (**1**), [Ni(μ$_{1,5}$-dca)(dca)(medpt)]$_2$ (**2**), and (μ-terephthalato)[Ni(dca)(dpt)(H$_2$O)]$_2$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{20}H_{34}N_{18}Ni_2$	$C_{22}H_{38}N_{18}Ni_2$	$C_{24}H_{36}N_{12}Ni_2O_6$
Molecular mass	644.07	336.06	706.03
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	*P*-1 (n°2)	*Pbca ba-c* (n° 61)
a [Å]	8.424(7)	7.677(3)	9.096(1)
b [Å]	9.368(11)	8.380(2)	13.229(1)
c [Å]	10.589(5)	12.238(3)	26.824(1)
α [°]	84.15(7)	80.24(2)	90.0
β [°]	79.83(5)	78.63(2)	90.0
γ [°]	66.33(9)	82.98(3)	90.0
V [Å^3]	752.9(11)	757.5(4)	3227.8(4)
Z	1	2	4
T [K]	293(2)	293(3)	293
λ(Mo-*K*α) [Å]	0.71069	0.71073	0.71069
$d_{calcd.}$ [Mg·m^{-3}]	1.421	1.473	1.453
μ(Mo-*K*α) [mm^{-1}]	1.294	1.290	1.223
R[a]	0.0422	0.0482	0.0458
$R^2\omega$[b]	0.0742	0.1263	0.1106

[a] $R(F_o) = \Sigma F_o - F_c / \Sigma F_o$ [b] $R\omega(F_o)^2 = \{\Sigma\{\omega[(F_o)^2 - (F_c)^2\}^2]/\Sigma\{\omega[(F_o)^2]^2\}^{1/2}$

CCDC-200891 (**1**), -200892 (**2**), and -200894 (**3**) 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].

Acknowledgments

This research was partially supported by CICYT (Grant BQU2000/0791) and the Council of Scientific and Industrial Research, New Delhi, India (Granted to NRC).

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[1] S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.* **1998**, 439.
[2] M. Kurmoo, C. J. Kepert, *New. J. Chem.* **1998**, 1515.
[3] J. L. Manson, C. R. Kmety, Q. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein, J. S. Miller, *Chem. Mater.* **1998**, *10*, 2552.
[4] J. L. Manson, C. R. Kmety, A. J. Epstein, J. S. Miller, *Inorg. Chem.* **1999**, *38*, 2552.
[5] S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray, D. J. Price, *J. Chem. Soc., Dalton Trans.* **1999**, 2987.
[6] P. Jensen, S. R. Batten, G. D. Fallon, D. C. R. Hockless, B. Moubaraki, K. S. Murray, R. Robson, *J. Solid State Chem.* **1999**, *145*, 387.
[7] J. L. Manson, D. W. Lee, A. L. Rheingold, J. S. Miller, *Inorg. Chem.* **1998**, *37*, 5966.
[8] J. L. Manson, C. D. Incarvito, A. L. Rheingold, J. S. Miller, *J. Chem. Soc., Dalton Trans.* **1998**, 3705.
[9] J. L. Manson, A. M. Arif, J. S. Miller, *J. Mater. Chem.* **1999**, *9*, 979.
[10] A. Escuer, F. A. Mautner, N. Sanz, R. Vicente, *Inorg. Chem.* **2000**, *39*, 1668.
[11] J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold, J. S. Miller, *J. Solid State Chem.* **1999**, *145*, 369.
[12] A. Claramunt, A. Escuer, F. A. Mautner, N. Sanz, R. Vicente, *J. Chem. Soc., Dalton Trans.* **2000**, 2627.
[13] J. Carranza, C. Brennan, J. Sletten, F. Lloret, M. Julve, *J. Chem. Soc., Dalton Trans.* **2002**, 3164.
[14] A. Escuer, F. A. Mautner, N. Sanz, R. Vicente, *Inorg. Chim. Acta* **2002**, *340*, 163.
[15] S. R. Marshall, C. D. Incarvito, J. L. Manson, A. L Rheingold, J. S. Miller, *Inorg. Chem.* **2000**, *39*, 1969.
[16] B.-W. Sun, S. Gao, B.-Q. Ma, Z.-M. Wang, *New J. Chem.* **2000**, *24*, 953.
[17] I. Riggio, G. A. van Albada, D. D. Ellis, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2001**, *313*, 120.
[18] S. Martín, M. G. Barandika, J. I. Ruiz de Larramendi, R. Cortés, M. Font-Bardía, L. Lezama, Z. E. Serna, X. Solans, T. Rojo, *Inorg. Chem.* **2001**, *40*, 3687.
[19] J. L. Manson, Q.-Z. Huang, J. W. Lynn, H.-J. Koo, M.-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyriou, J. S. Miller, *J. Am. Chem. Soc.* **2001**, *123*, 162.
[20] P. Jensen, S. R. Batten, B. Moubaraki, K. S. Murray, *J. Solid State Chem.* **2001**, *159*, 352.
[21] P. Jensen, S. R. Batten, B. Moubaraki, K. S. Murray, *J. Chem. Soc., Dalton Trans.* **2002**, 3712.
[22] A. Escuer, R. Vicente, X. Solans, M. Font-Bardía, *Inorganic Chemistry* **1994**, *33*, 6007.
[23] R. Vicente, A. Escuer, J. Ferretjans, H. Stoeckli-Evans, X. Solans, M. Font-Bardía, *J. Chem. Soc., Dalton Trans.* **1997**, 167.
[24] B. Vangdal, J. Carranza, F. Lloret, M. Julve, J. Sleten, *J. Chem. Soc., Dalton Trans.* **2002**, 566.
[25] P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, E. H.-K. Tan, *Polyhedron* **2001**, *20*, 1129.
[26] P. Jensen, S. R. Batten, B. Moubaraki, K. S. Murray, *Chem. Commun.* **2000**, 793.
[27] C. P. Landee, D. M. Mudgett, B. M. Foxman, *Inorg. Chim. Acta* **1991**, *186*, 45.
[28] J. Cano, G. De Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, A. Caneschi, *J. Chem. Soc., Dalton Trans.* **1997**, 1915.
[29] G. M. Sheldrick, SHELXS, Program for the Solution of Crystal Structure. University of Gottingen, Germany, **1997**.
[30] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure. University of Gottingen, Germany, **1997**.
[31] International Tables of X-ray Crystallography, **1974**. Ed. Kynoch press, vol. IV, pp 99−100 and 149.
[32] Collaborative Computational Project, Number 4. *Acta Crystallogr., Sect. D* **1994**, *50*, 760.
[33] G. M. Sheldrick, SHELX-97: *Programs for Crystal Structure Analysis (Release 97−2).* University of Göttingen, Germany, **1998**.
[34] WinGX: A Windows Program for Crystal Structure Analysis., L. J. Farrugia, University of Glasgow, Glasgow, **1998**.

Received January 16, 2003