Unusual Two-Dimensional Nickel(II) Complexes Based on $[Ni(dien)]^{2+}$ and $[M(CN)_4]^{2-}$ Building Blocks (M = Ni, Pd and Pt) − Synthesis, Structural Diversity and Magnetic Properties

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Three novel polymeric compounds $[Ni(dien)Ni(CN)_4]_n(H_2O)_n$ (**1**), $[Ni(dien)Pd(CN)_4]_n$ (**2**), and $[Ni(dien)Pt(CN)_4]_n$ (**3**) were synthesised by reaction of $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](PF_6)_2$ with $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) in aqueous solution. The structure of these compounds contains two $[Ni(dien)]^{2+}$ cationic units bridged by two $[M(CN)_4]^{2-}$ anions in a *cis* fashion, generating a square-shaped $[Ni_2–M_2]$ metal core. The different linking modes between the cores afford a 2D bilayer with encapsulated water in compound **1** and corrugated layers in compounds **2** and **3**. These coordination modes are compared to the different bridging modes of tetracyanometalate-containing compounds retrieved from the CSD database. The three compounds present a very weak antiferromagnetic coupling between the octahedrally coordinated Ni^{II} ions.
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Introduction

The design and synthesis of molecular magnetic materials have been the focus of increasing attention over the past three decades.[1] So, the study of magnetic interactions in di- and polynuclear complexes, as a function of structural and electronic factors, is still a main challenge in inorganic chemistry. Significant research has been devoted to analyzing the role of the cyanide group as a bridging ligand, both from an experimental[2] and a theoretical[3] point of view. Because it is a good exchange pathway between paramagnetic centres, it is widely employed in the preparation of molecular magnetic materials.[4]

Cyanometalate anions have been extensively used as design elements in supramolecular systems, where they can act as bridging ligands to form high dimensionality coordination polymers with transition metal cations.[5] An approach to the synthesis of these materials is the use of $[M(CN)_4]^{2-}$ groups in conjunction with a transition-metal-ion complex, due to the ability of the cyanide group to connect various central atoms, for building molecular assemblies with various degrees of dimensionality. As can be seen in Table 1, a wide structural diversity can be found in compounds containing bridging tetracyanometalate anions.[6] In this context, it is worth underlining the works of Shore et al.[7] on polymeric systems based on lanthanides, with a variety of Lewis bases and tetracyanometalate anions, and those of Long et al.[8] on cubic-cluster systems. Furthermore, some Hofmann clathrates present cooperative spin-crossover behaviour.[9]

The work described here is part of our research program on the chemistry of first-row transition metal oxalate and cyanide complexes.[10] We employed the nickel dinuclear precursor, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](PF_6)_2$, due to the lability of its water molecules, which may be replaced by a plethora of ligands. In this paper we report the synthesis, vibrational study, crystal structure and magnetic properties of the following polymeric compounds: $[Ni(dien)Ni(CN)_4]_n(H_2O)_n$ (**1**), $[Ni(dien)Pd(CN)_4]_n$ (**2**), and $[Ni(dien)Pt(CN)4]_n$ (**3**), obtained from the above-mentioned precursor and the cyano complexes $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$, respectively.

Results and Discussion

Synthesis and Spectroscopic Studies

In the synthesis of Ni^{II} complexes based on bridging oxalate and tetracyanometalates, the dinuclear cationic complex $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]^{2+}$ was used as a precursor, owing to the lability of its water molecules, which may be substituted by a plethora of ligands, such as pseudohalide ligands and cyanometalates. As can be seen in Scheme 1, the reaction of the precursor with $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) gives at first an insoluble precipitate, which correspond to the polymeric compounds $[\{Ni(dien)M(CN)_4\}]_n$, and then the trinuclear molecular compounds $[\{Ni(dien)\}_2(\mu\text{-ox})\{M(CN)_4\}]$.[6d,10b] The formation of com-

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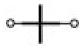
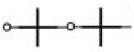
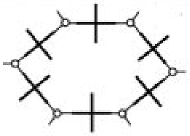
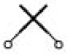
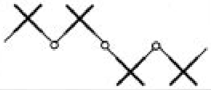
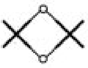
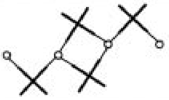
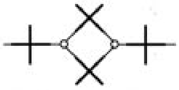
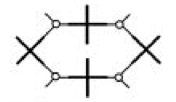
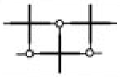
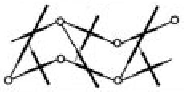
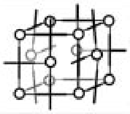
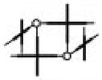
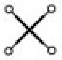
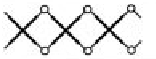
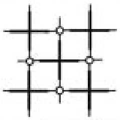
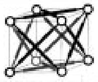
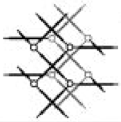
Table 1. Bridging modes of group 10 tetracyanometalates

Structure	Description[a]	No.	Ref.
Coordination 2			
	*trans* 0D, trinuclear monomer $[M'MM']$; M: Ni, Pt; M': Fe, Re, Ho $[\{Fe(dppe)(Cp)\}_2\{Pt(CN)_4\}]$ (QAFLAK)	3	6a
	*trans* 1D, chain $[M'M]_n$; M: Ni, Pd, Pt; M': Ni, Cu, Ag, Sm, Yb $[Cu(en)_2\{Ni(CN)_4\}]_n$ (HEGBIE)	11	6b
	*trans* 2D, plane $[M'_6M_6]_n$; M: Ni, Pt; M': Eu, Yb $[Eu(dmf)_5\{Ni(CN)_4\}]_n$ (YEQRIV)	2	6c
	*cis* 0D, trinuclear monomer $[M'MM']$; M: Ni, Pd, Pt; M': Ni, Cu $[\{Ni(dien)\}_2\{Ni(CN)_4\}(ox)]$ (RIHBEP)	4	6d
	*cis* 1D, chain $[M'M]_n$; M: Ni; M': Ni $[Ni(en)_2\{Ni(CN)_4\}]_n$ (SIFKOH)	1	6e
	double *cis* 0D, tetranuclear monomer $[M'M_2M']$; M: Pt; M': Cu $[\{Cu(bpy)(H_2O)\}_2\{Pt(CN)_4\}_2]$ (HIPHOD)	1	6f
	*cis*-double *cis* 1D, chain $[M'M_2M'M]_n$; M: Pd, Pt; M': Nd, Eu $[\{Nd(H_2O)_6\}_2\{Pd(CN)_4\}_3]_n$ (PIJPON)	2	6g
	*trans*-double *cis* 1D, chain $[M'M_2M'M]_n$; M: Ni, Pd; M': Ce, Sm, Eu, Er, Yb $[Yb(H_2O)(dmf)_4\}_2\{Pd(CN)_4\}_3]_n$ (GOMTUX)	7	6h
	double *trans*-double *cis* 1D ladder $[M'_4M_4]_n$; M: Ni, Pd, Pt; M': Y, Sm, Eu, Gd, Ho, Yb $[Sm(dmf)_5\}_2\{Pd(CN)_4\}_3]_n$ (JAQBOS)	7	6i

Structure	Description[b]	No.	Ref.
Coordination 3			
	1D, ladder $[M'M]_n$; M: Ni, Pt; M': Eu $[Eu(dmf)_4\{Ni(CN)_4\}]_n$ (TOJXIZ)	2	6j
	2D, bilayer $[M'_3M_3]_n$; M: Ni; M': Cu $[Cu(dap)\{Ni(CN)_4\}]_n$ (WODBAS)	1	6k
	3D, cubic cluster $[M'_{12}M_{12}]$; M: Ni; M': Cr $[\{Cr(Me_3\text{-}tacn)\}_{12}\{Ni(CN)_4\}_{12}]^{12+}$ (OFOQUV)	1	6l
	2D, bilayer $[M'_2M_2]$; M: Ni; M': Ni $[Ni(dien)\{Ni(CN)_4\}]_n$ (1)	1	This work
Coordination 4			
	0D nonanuclear monomer $[M'_4M]$; M: Ni; M': Ni $[\{Ni_2L(CN)\}_4\{Ni(CN)_4\}]^{6+}$ (NEPFAP)	1	6m
	1D, chain $[M'M_2M']$; M: Ni; M': Cu $[\{Cu(medpt)\}_2Ni(CN)_4\}]_n{}^{2n+}$ (RAKJUI)	2	6n
	2D, plane $[M'M]_n$; M: Ni; M': Mn, Fe, Ni $[Fe(NH_3)_2\{Ni(CN)_4\}]_n$ (COQSAC)	7	6o
	3D, cubic cluster $[M'_8M_6]$; M: Ni; M': Cr, Mo $[\{Cr(Me_3\text{-}tacn)\}_8\{Ni(CN)_4\}_6]^{12+}$ (RAHYOO)	7	2a
	3D network $[M'M]_n$; M: Pt; M': Cu $[Cu\{Pt(CN)_4\}]_n{}^n$ (JEJFAF)	1	6p

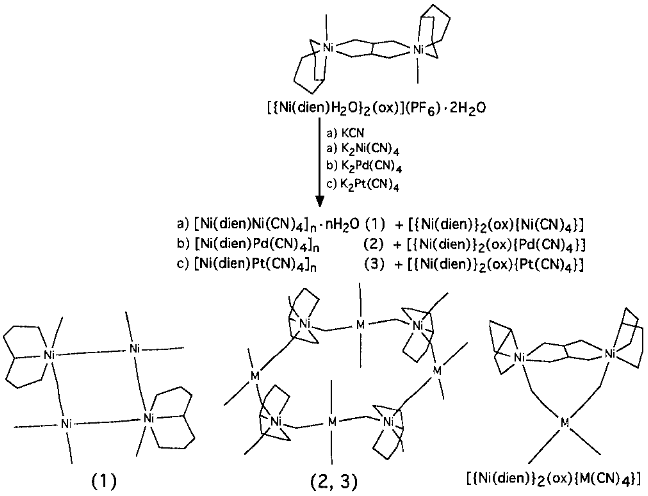
[a] Coordination mode, dimensionality, abbreviated formula, example, CSD refcode. [b] Dimensionality, abbreviated formula, example, CSD refcode

pound **1**, by using KCN as starting material, is probably a consequence of the high stability of the $[Ni(CN)_4]^{2-}$ complex, which leads to the initial formation of the tetracyanonickelate(II) anion when cyanide salt is added to a solution of the precursor.

The IR and Raman spectra of the compounds displaying the stretching vibrations associated to the CN group are shown in Figure 1. The similitude between the spectra of compounds **2** and **3** suggests that the coordination modes of the tetracyanometalate anions are very similar and quite different from that observed in compound **1**. Besides, as the number of independent $[M(CN)_4]^{2-}$ groups increases (one for **1** and two for **2** and **3**), the number of CN stretching-vibration bands also becomes greater.

Crystal Structures

The crystal structures of the compounds present two-dimensional arrangements, based on $[Ni(dien)]^{2+}$ cationic fragments, bridged by $[M(CN)_4]^{2-}$ groups.



Scheme 1

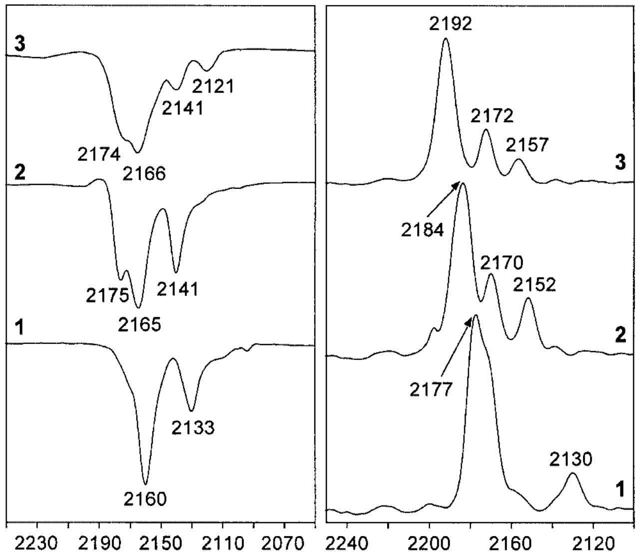


Figure 1. IR (left) and Raman (right) spectra of the compounds

[Ni(dien){Ni(CN)$_4$}]$_n$(H$_2$O)$_n$ (1)

The asymmetric unit of compound **1** consists of one [Ni(dien)]$^{2+}$ unit, one [Ni(CN)$_4$]$^{2-}$ anion and a water molecule, as illustrated in Figure 2. Selected bond lengths and angles are listed in Table 2. The structure of this compound contains two [Ni(dien)]$^{2+}$ cationic groups, bridged by two [Ni(CN)$_4$]$^{2-}$ anions in a *cis* fashion, generating a square-shaped [Ni$_2$−Ni$_2$] metal core. Each core is linked to another four cores through cyano groups, creating a two-dimensional bilayer parallel to the (011) plane (see Figure 3). In this arrangement, the distorted octahedral environment of Ni1 is set up by three nitrogen atoms from a diethylenetriamine ligand in *fac* and three nitrogen atoms from the corresponding cyanide ligands; thereby, each tetracyanonickelate anion connects three [Ni(dien)]$^{2+}$ moieties and the remaining uncoordinated cyano groups are parallel or antiparallel to the [100] direction giving rise to CN-rich hydrophilic regions (see Figure 4). The water molecule remains encapsulated inside the bilayer and is weakly hydrogen-bonded to the N atoms of the dien ligands. The bilayers are held together by hydrogen bonds, which involve the N1 and

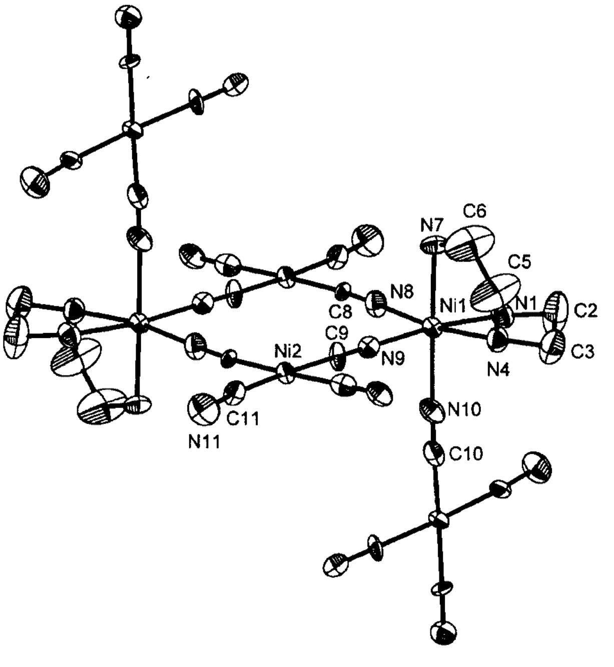


Figure 2. ORTEP view of the metallic core in compound **1** together with the atom labelling

Table 2. Selected bond lengths [Å] and angles [°] for compounds **1**−**3**

Compound	**1**	**2**	**3**
Ni1 coordination sphere:			
Ni1−N1	2.099(7)	2.125(4)	2.12(2)
Ni1−N4	2.104(8)	2.116(4)	2.12(2)
Ni1−N7	2.093(7)	2.074(4)	2.09(2)
Ni1−N8	2.056(9)	2.058(4)	2.09(2)
Ni1−N9	2.099(9)	2.108(4)	2.13(2)
Ni1−N10	2.095(9)	2.106(4)	2.14(2)
N1−Ni1−N4	81.8(3)	81.4(2)	80.7(6)
N1−Ni1−N7	94.8(3)	94.5(2)	95.7(6)
N1−Ni1−N8	92.0(3)	91.7(2)	92.9(6)
N1−Ni1−N9	172.8(3)	168.8(2)	168.8(7)
N1−Ni1−N10	86.2(3)	84.2(2)	83.3(6)
N4−Ni1−N7	81.8(3)	82.2(2)	82.4(6)
N4−Ni1−N8	170.7(3)	168.4(2)	168.5(6)
N4−Ni1−N9	92.5(3)	90.7(2)	91.9(5)
N4−Ni1−N10	95.6(3)	99.3(2)	98.8(6)
N7−Ni1−N8	92.1(3)	89.0(2)	88.8(6)
N7−Ni1−N9	88.6(3)	92.3(2)	91.7(6)
N7−Ni1−N10	177.0(3)	177.7(2)	178.3(5)
N8−Ni1−N9	94.3(3)	97.4(2)	95.7(6)
N8−Ni1−N10	90.8(3)	89.2(2)	89.9(6)
N9−Ni1−N10	90.1(3)	89.3(2)	89.4(6)
Ni coordination plane:			
Ni2−C8	1.86(1)		
Ni2−C9	1.853(9)		
Ni2−C10	1.84(1)		
Ni2−C11	1.857(9)		
C8−Ni2−C9	87.6(4)		
C8−Ni2−C10	177.5(4)		
C8−Ni2−C11	93.3(4)		
C9−Ni2−C10	90.0(4)		
C9−Ni2−C11	177.3(5)		
C10−Ni2−C11	89.1(4)		
Pd and Pt coordination planes:		M = Pd	M = Pt
M1−C9		2.013(4)	1.97(2)
M1−C10		1.990(4)	1.99(2)
M2−C8		1.989(5)	2.01(1)
M2−C11		1.988(5)	1.98(2)
C9−M1−C10		91.0(2)	92.4(8)
C9−M1−C9′		180.0(2)	180.0(6)
C9−M1−C10′		89.0(2)	87.6(8)
C10−M1−C10′		180.0(−)	180.0(−)
C8−M1−C11		85.9(2)	95.3(9)
C8−M1−C8′		180.0(3)	180.0(9)
C8−M1−C11′		94.1(2)	84.7(9)
C11−M1−C11′		180.0(−)	180.0(−)

N7 atoms belonging to the same dien ligand and the N11 atom of the uncoordinated cyano group (see Table 3).

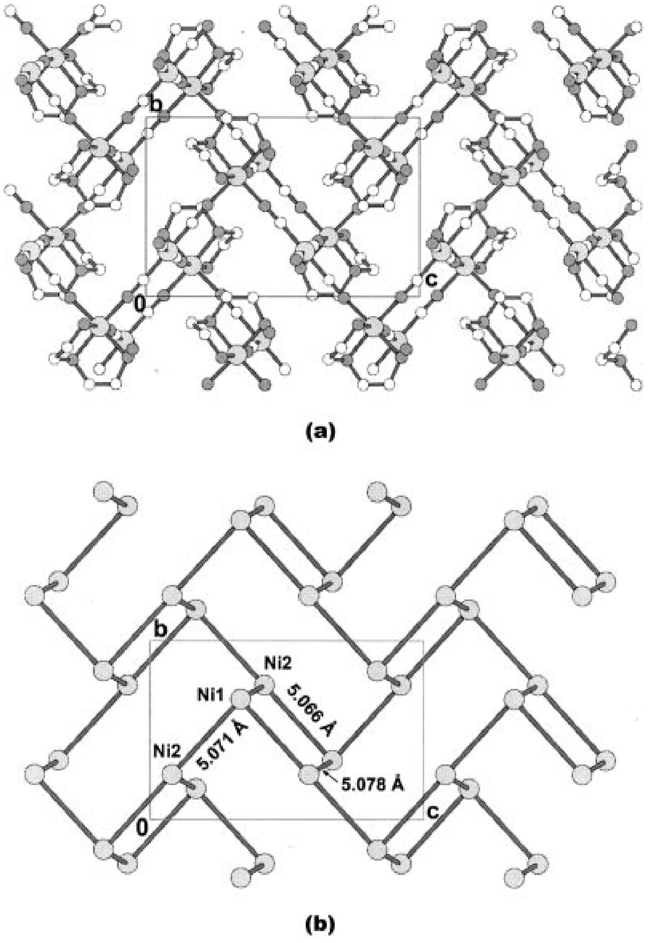


Figure 3. Compound **1**: (a) projection along the *a* axis of the bilayer; (b) metallic skeleton formed by cyanide-bridged Ni atoms with indication of the Ni···Ni distances shorter than 6 Å (water molecules are omitted for clarity)

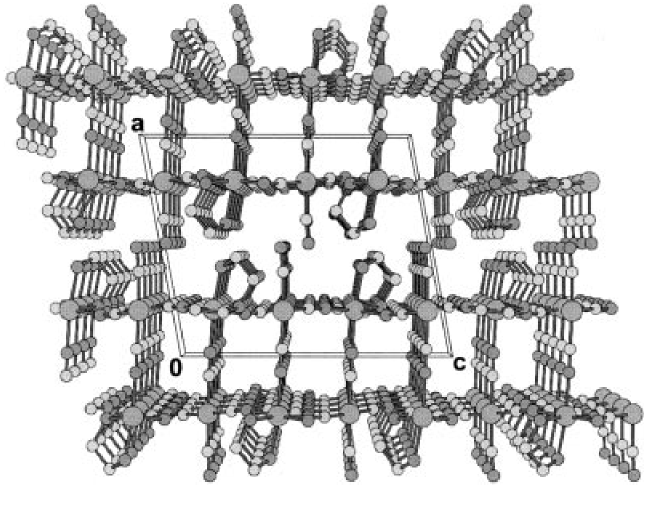


Figure 4. Perspective view of compound **1** along the *b* axis showing the cyanide terminal-rich area between two adjacent bilayers

Table 3. Hydrogen contacts for compounds **1**−**3**

	1		**2**	**3**
N1···N11[a]	3.13(1)	N1···N11[b]	3.488(7)	3.54(3)
N4···O1 (intra)	3.114(9)	N4···N10[c]	3.383(6)	3.36(2)
N7···N11[a]	3.184(9)	N7···N11[d] (intra)	3.050(6)	3.04(3)
N7···O1[e] (intra)	3.44(1)	N7···N11[b]	3.152(7)	3.12(3)

[a] Symmetry codes: $1 + x, y, z$. [b] $1 - x, 2 - y, 1 - z$. [c] $1 - x, 1 - y, 2 - z$. [d] $x, y - 1, z$. [e] $x, 1/2 - y, z - 1/2$; "intra" means intralamellar hydrogen bonds.

[Ni(dien){Pd(CN)$_4$}]$_n$ (2) and [Ni(dien){Pt(CN)$_4$}]$_n$ (3)

Compounds **2** and **3** are isostructural and the asymmetric unit of both consists of one *fac*-[Ni(dien)]$^{2+}$ cationic group and two centrosymmetric [M(CN)$_4$]$^{2-}$ anions, as illustrated in Figure 5 [M = Pd (**2**), Pt (**3**)]. Selected bond lengths and angles are listed in Table 2. The repeating molecular unit of **2** and **3** is similar to that of compound **1**: two [Ni(dien)]$^{2+}$ moieties bridged by two [M(CN)$_4$]$^{2-}$ anions in a *cis* mode, generating a [Ni$_2$−M$_2$] metal core. Nevertheless, some differences between the two metallic cores, concerning the dien orientation around the nickel atoms, can be appreciated. Thus, in compound **1**, the N4 dien atom occupies an equatorial position with respect to the metallic core, whereas in compounds **2** and **3** its position is axial. Moreover, these metallic cores form ribbons running along the [010] direction, where each tetracyanometalate(II) group connects four [Ni(dien)]$^{2+}$ cations, as in compound {[{Cu(medpt)}$_2$Ni(CN)$_4$](ClO$_4$)$_2$}$_n$.[6n] These ribbons are linked by [M(CN)$_4$]$^{2-}$ anions that are bound to the Ni^{2+} centres through the cyanide bridges in a *trans* fashion to generate a puckered sheet along the (011) plane (see Figure 6). The 2D planes are connected by hydrogen bonds in a weakly held 3D array (see Figure 7), which involves all dien N atoms and the uncoordinated N11 atoms of the M2 centres together with the N10 atom (see Table 3).

Bridging Modes of [M(CN)$_4$]$^{2-}$ Anions

A total of 60 compounds, containing tetracyanometalates as bridging units, were retrieved from the Cambridge Structural Database. Table 1 summarizes their bridging modes and main features (coordination modes, dimensionality, abbreviated formula and CSD refcode of a representative example). More than half present coordination 2, a bridging mode that usually gives 1D arrangements, in which the metal is usually a lanthanide. Coordination 3 is only present in four cases with variable dimensionality. Although compound **1** shows coordination 3, its structure stands for a new packing mode. Coordination 4 is mainly present in cubic clusters and square-planar arrangements. On the other hand, in compounds **2** and **3**, the tetracyanometalate anions present two coordination modes, 4 to form ribbons along one direction and 2 in order to connect the ribbons in a corrugated layer.

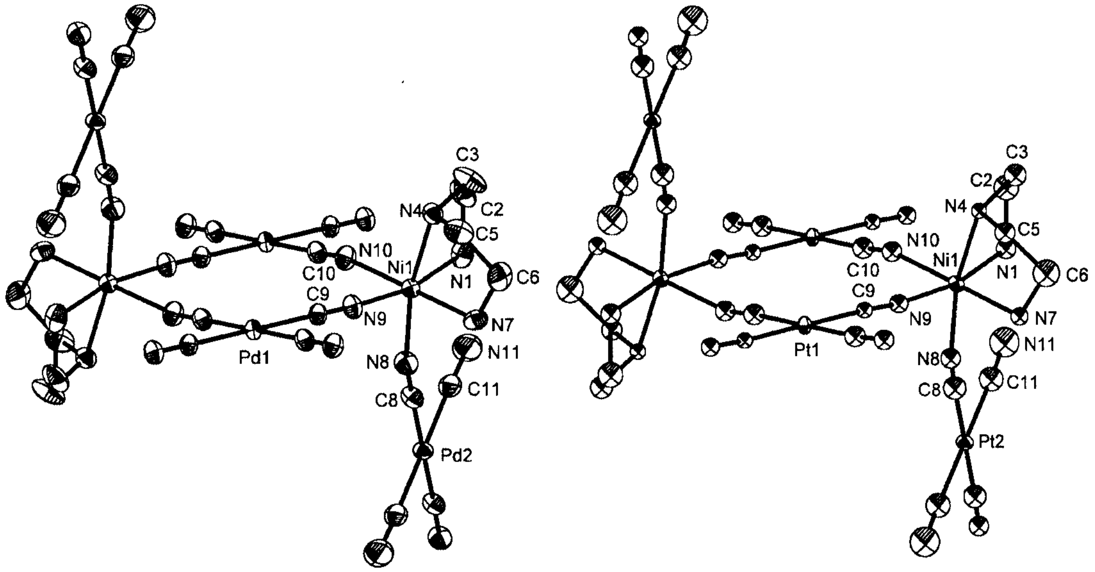


Figure 5. ORTEP views of the metallic core in compounds **2** (left) and **3** (right)

Magnetic Measurements

The temperature dependence of the magnetic susceptibilities of compounds **1**−**3** was measured in the temperature range 5−300 K. Plots of χ_mT and $\chi_m^{-1}T$ vs. T were deposited (see Supporting Information). The thermal evolution of χ_m satisfies the Curie−Weiss law at high temperatures. The values of C and θ are equal to 1.14 $cm^3{\cdot}K{\cdot}mol^{-1}$ and −0.8 K, respectively, for compound **1**, 1.13 and −0.9 for **2** and 1.16 and −0.6 for **3**. These results, together with the continuous decrease in the χ_mT values, is indicative of antiferromagnetic exchange coupling in the compounds. On the basis of the crystal structures, the compounds were treated as 2D square-planar Heisenberg systems with S = 1 and only magnetic interactions between the nickel(II) ions inside the layers were considered. It was possible to fit the χ_m experimental values using the analytical expression reported by Lines[11] for a 2D square-planar Heisenberg system, from a high-temperature expansion series studied by Rushbrooke and Wood [Equation (1)], where $x = J/kT$, A = 5.333333, B = 9.777778, C = 9.481482, D = 19.06173, E = 45.08971, F = 25.46392.[12]

$$\chi = \frac{2Ng^2\beta^2}{3kT}\left[1 + Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5 + Fx^6\right]^{-1} \qquad (1)$$

The least-squares fittings to the experimental data (J = −0.10 cm^{-1} and g = 2.134 for compound **1**, −0.11 and 2.127 for **2** and −0.08 and 2.150 for **3**) show the presence of very weak antiferromagnetic interactions between the paramagnetic nickel ions within each layer through the diamagnetic $[M(CN)_4]^{2-}$ groups.

On the other hand, octahedrally coordinated Ni^{II} compounds frequently exhibit large zero-field splittings of the $^3A_2$ ground state that, qualitatively, produce similar effects to those of antiferromagnetic interactions. In this sense, we have tried to fit the experimental data to the analytical equation for magnetic susceptibility, calculated by application of van Vleck's equation. However, no satisfactory fit could be obtained using that expression and the calculated curves show that the experimental decrease of the magnetic effective moment starts at higher temperatures that those predicted by this simple model (deposited as Supporting Information). Therefore, we can conclude that magnetic exchange is the dominant term in the magnetic properties of compounds **1**−**3**, even if the obtained J values could be somewhat overestimated, due to the possible influence of the Ni^{II} single-ion zero-field splitting.

Conclusions

The reaction between group 10 tetracyanometalates and the cationic complex $[\{Ni(dien)(H_2O)\}_2(\mu\text{-}ox)]^{2+}$ leads to the formation of the title polymeric compounds, followed by the trinuclear molecular compounds $[\{Ni(dien)\}_2(\mu\text{-}ox)\{M(CN)_4\}]$. Compound **1** contains an encapsulated water molecule, while compounds **2** and **3** are anhydrous and isostructural.

The repeating molecular unit for the three compounds consists of two $[Ni(dien)]^{2+}$ cationic building blocks bridged by two $[M(CN)_4]^{2-}$ anions in a *cis* mode, generating a $[Ni_2{-}M_2]$ metal core. Nevertheless, some structural differences between both metallic cores could be appreciated, concerning the dien orientation around the nickel atoms and the dihedral angle between the metallic core and the $[M(CN)_4]^{2-}$ groups. This fact could be explained by the different types of hydrogen-bonding present in the compounds, which are strongly influenced by the presence of the water molecule of compound **1**.

These compounds present two novel bridging modes for tetracyanometalate groups. Compound **1** could be used as

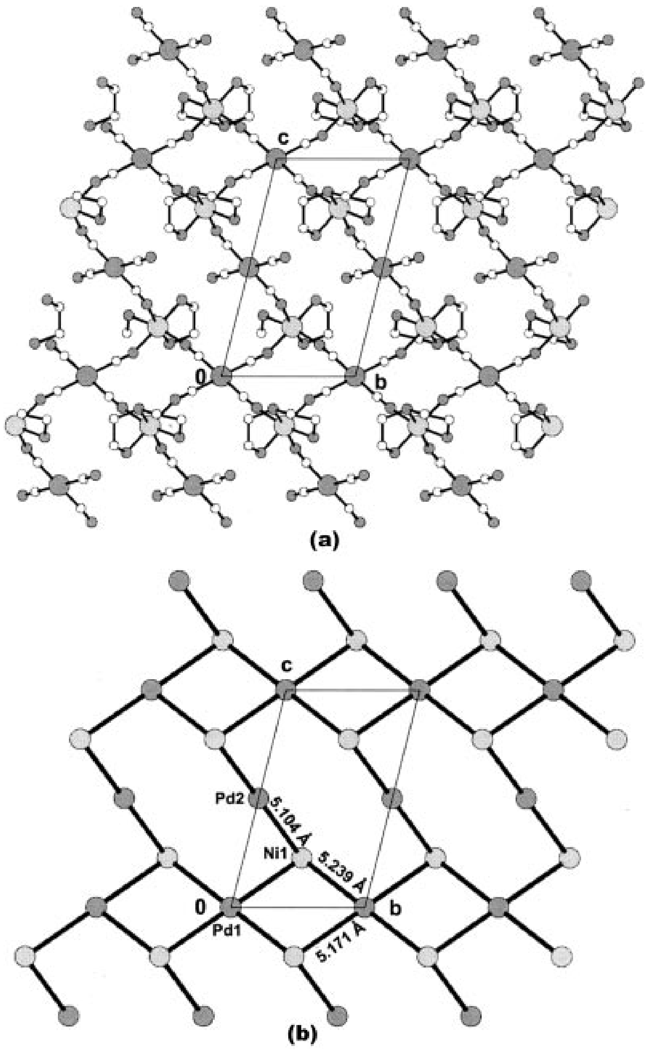


Figure 6. Compound **2**: (a) projection along the *a* axis of a corrugated layer; (b) metallic skeleton formed by cyanide-bridged Ni and Pd atoms with indication of the Ni···Pd distances shorter than 6 Å

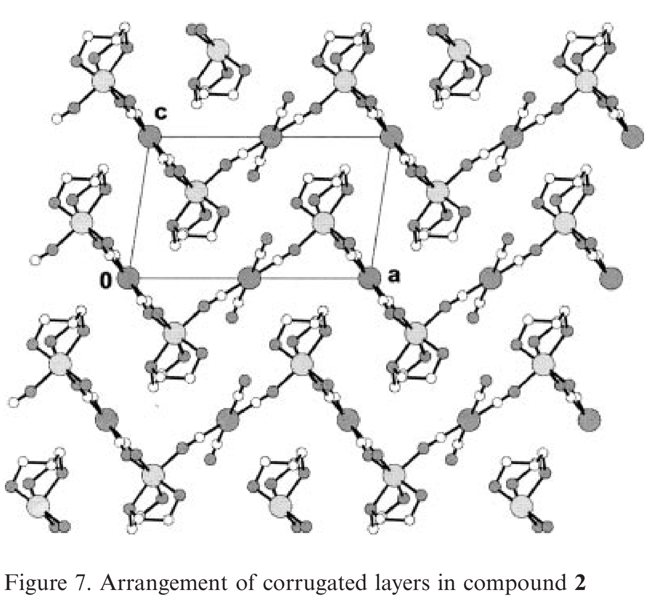


Figure 7. Arrangement of corrugated layers in compound **2**

an intercalation precursor, due to the special arrangement of the uncoordinated cyanide groups of the $[Ni(CN)_4]^{2-}$ anions. On the other hand, compounds **2** and **3** present two types of bridging modes for the tetracyanometalate groups (coordination numbers 2 and 4), giving rise to a structure containing corrugated layers.

The very low values in the coupling constants confirm the poor exchanging capabilities of the tetracyanometalate groups.

Experimental Section

General: Potassium cyanide (KCN; Fluka), potassium tetracyanonickelate {$K_2[Ni(CN)_4]$; Aldrich}, potassium tetracyanopalladate {$K_2[Pd(CN)_4]$; Aldrich}, and potassium tetracyanoplatinate {$K_2[Pt(CN)_4]$; Aldrich} were used as purchased without further purification. The complex $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](PF_6)_2$ was prepared using a previously described method.[13] Infrared spectra for solid samples were obtained as KBr pellets with a Mattson 1000 FT-IR spectrometer. Raman spectra were measured as pressed pellets using a dispersive micro-probe Renishaw spectrometer, equipped with a high-power 785 nm excitation laser of 500 mW nominal output power. Filters were used to reduce the laser power at the sample to 10 or 1 %. For each spectrum 5−10 scans were collected and the acquisition times ranging from 100 to 300 s. Magnetic susceptibility measurements on polycrystalline samples were performed in the temperature range 5−300 K with a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field used in the experiments was of 0.1 T, a value at which the magnetization versus magnetic-field curve was still linear at 5.0 K. Experimental susceptibility values were corrected for the diamagnetic contributions of the constituent atoms, evaluated from Pascal's constants ($-185\cdot10^{-6}$, $-187\cdot10^{-6}$ and $-201\cdot10^{-6}$ cm^3/mol for compounds **1**−**3**, respectively), and for the temperature-independent paramagnetism (estimated to be $200\cdot10^{-6}$ cm^3/mol).

Synthesis of $[Ni(dien)\{Ni(CN)_4\}]_n(H_2O)_n$ (1): This compound precipitated as a highly insoluble pink residue when KCN (0.25 g, 3.84 mmol) was added, whilst stirring, to an aqueous solution (50 mL) of the precursor complex, $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})](PF_6)_2$ (1.42 g, 1.84 mmol). An alternative method involved mixing aqueous solutions of $K_2[Ni(CN)_4]$ (0.058 g, 0.24 mmol) and the precursor (0.36 g, 0.475 mmol). After removing the pink precipitate by filtration, the solvent was refluxed for 20 min and single crystals of compound **1** appeared after one week, yield 0.062 g (75%). $C_8H_{13}N_7Ni_2\cdot H_2O$ (342.69): calcd. C 28.04; H 4.41; N 28.61; found C 27.54; H 4.26; N 28.44.

Synthesis of $[Ni(dien)\{Pd(CN)_4\}]_n$ (2): This compound was obtained as a insoluble pink residue when the precursor (0.25 g, 0.324 mmol) was added to an aqueous solution (20 mL) of $K_2[Pd(CN)_4]$ (0.115 g, 0.40 mmol), yield 0.10 g (65%). Single crystals of this compound were obtained by slow diffusion in a test tube of a methanolic solution of $K_2[Pd(CN)_4]$, into an aqueous solution of the precursor. $C_8H_{13}N_7NiPd$ (372.36): calcd. C 25.81; H 3.52; N 26.33; found C 25.56; H 3.58; N 26.08.

Synthesis of $[Ni(dien)\{Pt(CN)_4\}]_n$ (3): Following the same procedure, compound **3** was prepared as a violet precipitate by using $K_2[Pt(CN)_4]$ (0.051 g, 0.136 mmol) and the precursor (0.25 g, 0.324 mmol), yield 0.035 g (55%). Single crystals of compound **3** were obtained by slow diffusion in a test tube of a methanolic solution of $K_2[Pt(CN)_4]$ into an aqueous solution of the precursor.

$C_8H_{13}N_7NiPt$ (461.05): calcd. C 20.84; H 2.84; N 21.27; found. C 20.55; H 3.00; N 20.94.

X-ray Crystallographic Studies: Single crystals suitable for X-ray analysis were obtained for the three compounds. Data collections for **1** and **3** were performed with a STOE IPDS diffractometer, equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and an image-plate detector. A total of 200 frames (oscillation range of 1°/frame and exposure time 5 min/frame) were collected, which were processed and corrected for Lorentz and polarization effects with the Stoe IPDS X-RED software package.[14] Indexes and unit-cell refinement were based on all observed reflections from ten frames collected with an oscillation range of 1°/frame and exposure time of 3 min/frame. Data for compound **2** were taken at room temperature with an Xcalibur single-crystal diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å) fitted with a Sapphire CCD detector. A total of 764 frames of data were collected with an exposure time of 10 s/frame, using the ω-scan technique with a frame width of $\Delta\omega = 0.6°$. Data frames were processed (unit cell determination, intensity data integration and correction for Lorentz and polarization effects) using the CrysAlis software package.[15] Visual inspection of the frames collected clearly indicated that compounds **2** and **3** crystallize as non-merohedral twins in the triclinic space group $P\bar{1}$. For compound **2**, an initial orientation matrix and initial cell parameters were obtained by indexing and post-refinement with the CrysAlis software package. This orientation matrix only indexed ca.75 % of the total data. The reflections not indexed by this orientation matrix were then extracted from the measured CCD images and indexed. Both orientation matrices are related by a twofold rotation around the [100] direction in reciprocal space. All frames were then evaluated twice using the CrysAlis software. An HKLF4 reflection file was first output using the data from the major component to aid in the solution of the structure. After the structure was solved, both data sets were given different batch numbers for SHELXL-97 refinement with HKLF5. Overlapping reflections occur twice in the reflection list with the indices of both domains. The twin refinement was performed with SHELXL-97 using the data in HKLF5 format and refinement of batch scale factors. Symmetry-equivalent reflections were not merged (SHELXL-97 procedure); all measured intensities were treated as independent data in the refinement. The refinement resulted in a ratio of 77.0(2):23.0(2) for the two twin domains. Following the same procedure, but using the Stoe IPDS software, the twin law for compound **3** was determined and found to be the same as for **2**. Due to the lower quality of the data collected for compound **3**, only the intensities from the major component of the twin were used for solution and refinement of the structure. All structures were solved using a combination of Patterson and direct methods.[16] Either all non-hydrogen atoms (compounds **1** and **2**) or metal atoms only (compound **3**) were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms of the dien ligands were placed in calculated positions and refined with a riding model. SHELXL-97[17] was used for all structure refinements. Neutral atom scattering factors and anomalous dispersion factors were taken from the literature.[18] Experimental details and crystal data for compounds **1**−**3** are given in Table 4. The April 2003 release of the Cambridge Structural Database[19] was used in this work to obtain the different bridging modes of the group 10

Table 4. Crystal data and data collection parameters for compounds **1**−**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_8H_{13}N_7Ni_2\cdot H_2O$	$C_8H_{13}N_7NiPd$	$C_8H_{13}N_7NiPt$
Formula mass	342.69	372.36	461.05
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.439(3)	7.283(1)	7.289(2)
b [Å]	8.839(2)	7.437(1)	7.447(2)
c [Å]	13.747(3)	12.589(1)	12.553(3)
α [°]	90	75.01(1)	74.92(2)
β [°]	100.60(3)	80.01(1)	79.84(3)
γ [°]	90	83.7581)	84.27(3)
V [Å^3]	1366.2(5)	647.2(1)	646.6(2)
Z	4	2	2
F(000)	704	368	432
$D_{\text{calcd.}}$ [g·cm^{-3}]	1.666	1.911	2.368
Crystal shape	prism	prism	prism
Crystal colour	pale violet	violet	violet
Crystal size [mm]	0.20 × 0.15 × 0.10	0.21 × 0.16 × 0.07	0.16 × 0.15 × 0.04
Diffractometer	STOE IPDS	Xcalibur	STOE IPDS
Temperature [K]	293(2)	293(2)	293(2)
Radiation [Å]	0.71073	0.71073	0.71073
μ [mm^{-1}]	2.755	2.833	12.252
Monochromator	graphite	graphite	graphite
Scan mode	φ oscillation	ω	φ oscillation
θ limits [°]	2.75−25	2.84−30	2.84−30.38
hkl range	−13 to 13; −9 to 10; −16 to 16	−10 to 10; −10 to 10; −17 to 17	−10 to 10; −10 to 10; −17 to 16
No. of unique reflections	2389	6251	2675
No. of observed data	801 [$I = 2\sigma(I)$]	4746 [$I = 2\sigma(I)$]	1148 [$I = 2\sigma(I)$]
No. of parameters	158	158	82
$\Delta\rho_{max}/\Delta\rho_{min}$ [e·Å^{-3}]	0.43/−0.53	2.57/−0.93	2.95/−3.55
R_1 [obsd. rflns.]	0.0426	0.0476	0.0596
wR_2 [all rflns.]	0.0683	0.1300	0.1310

tetracyanometalates. All searches were restricted to those CSD entries that satisfied the following secondary search criteria: (a) error-free after CSD evaluation procedures, (b) no reported structural disorder and (c) perfect matching of their chemical and crystallographic connectivity representations. CCDC-220434 (**1**), -220435 (**2**), -220436 (**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].

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