Hexacyanometalate Molecular Chemistry: Di-, Tri-, Tetra-, Hexa- and Heptanuclear Heterobimetallic Complexes; Control of Nuclearity and Structural Anisotropy**

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Abstract: Following a bottom-up approach to nanomaterials, we present a rational synthetic route to high-spin and anisotropic molecules based on hexacyanometalate $[M(CN)_6]^{3-}$ cores. Part 1 of this series was devoted to isotropic heptanuclear clusters; herein, we discuss the nuclearity and the structural anisotropy of nickel(II) derivatives. By changing either the stoichiometry, the nature of the terminal ligand, or the counterion, it is possible to tune the nuclearity of the polynuclear compounds and therefore to control the structural anisotropy. We present the synthesis and the characterisation by mass spectrometry, X-ray crystallography and magnetic susceptibility of bi-, tri-, tetra-, hexa- and heptanuclear species $[M(CN)_n(CN{-}M'L)_{6-n}]^{m+}$ (with $n = 0-5$; $M = Cr^{III}$, Co^{III}, $M' = Ni^{II}$; L = pentadentate ligand). Thus, with $M = Cr^{III}$, d^3, $S = 3/2$, a dinuclear complex $[Cr^{III}(CN)_5(CN{-}NiL_n)]^{9+}$, ($L_n$ = polydentate ligand) was built and characterised, showing a spin ground state, $S_G = 5/2$, with a ferromagnetic interaction $J_{Cr,Cu} = +18.5\ cm^{-1}$. With $M = Co^{III}$ (d^6, $S = 0$) were built di-, tri-, tetra-, hexa and hepanuclear CoNi species: CoNi, $CoNi_2$, $CoNi_3$, $CoNi_5$ and $CoNi_6$. By a first approximation, they behave as one, two, three, five and six isolated nickel(II) complexes, respectively, but more accurate studies allow us to evaluate the weak antiferromagnetic coupling constant between two next-nearest neighbours M′-Co-M′.

Keywords: cyanides · high-spin molecules · magnetic properties · polynuclear complexes · structural anisotropy

Introduction

In the field of molecular magnetism[1], specific attention is devoted to polynuclear complexes with large-spin ground states and high anisotropy that exhibit original magnetism such as single-molecule magnet behaviour[2–4] (slow relaxation time of the magnetisation below a so-called blocking temperature, T_B) or magnetic quantum-tunnelling effects.[5, 6] The topic is both fundamental and applicable, due to potential storage of magnetic information at the molecular scale. To obtain a "single-molecule magnet", one must build a uniaxial system with an anisotropy barrier $E_a = DS_Z^2$ between the two degenerate $\pm M_S$ energy levels, where D is the zero-field splitting of the ground state, and S_Z is the projection of the spin along the anisotropy axis. The higher the barrier is, the higher the blocking temperature and the more efficient the single-molecule magnet. The other parameters to control are 1) the intramolecular exchange coupling J between paramagnetic ions in the cluster, which has to be significant to sufficiently separate the ground spin state from the excited states; 2) the intermolecular interaction zJ', where J' is the intermolecular exchange interaction, and z is the number of neighbouring clusters, which has to be negligible to avoid three-dimensional order and to observe the properties of the isolated nanoscale objects.

Among the four parameters to take into consideration in the design and the synthesis of the single-molecule magnets

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[**] Hexacyanometalate Molecular Chemistry, Part 2. For Part 1, see reference [7]; for Part 3, see reference [9].

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(S, D, J and zJ'), we have shown in Part 1[7] how to control the ground spin state S and how to reach spin values as high as 27/2 with a manganese derivative of hexacyanochromate(III), the octahedral ferrimagnetic $[Cr^{III}(CN-Mn^{II}(L)_6)]$ cluster. We observed also that the octahedral symmetry leads to negligible values of the anisotropy D. Indeed, the ground state anisotropy of a polynuclear cluster (uniaxial D, rhombic E and higher terms in the Hamiltonian) is a function of several parameters such as 1) the local anisotropy of each of the metallic ions; 2) the exchange anisotropy and 3) the overall structural anisotropy.[8] If the third, structural, parameter cannot be controlled by chemistry, it is futile to focus on the electronic ones. Thus herein we focus on the structural anisotropy and in particular on polynuclear complexes based on hexacyanometalates $[M(CN)_6)]$ ($M = Cr^{III}$ and Co^{III}), in which the nuclearity was varied from binuclear to heptanuclear, and nickel(II) species were used as Lewis acids associated with the cyanometalates.

Part 3[9] of this series is devoted to the study of the exchange coupling, through the description of several trinuclear $CrNi_2$ complexes. The study of electronic aspects of anisotropy based on high-frequency EPR of mononuclear and polynuclear complexes, and on magnetisation measurements on single crystals, are in progress and will be reported later.

Results and Discussion

The synthesis of new polynuclear complexes with large-spin ground states has been developed in our laboratory over several years.[10–15] Following a strategy that uses polyfunctionalised cores such as $[Cr(CN)_6]^{3-}$ as Lewis bases and mononuclear complexes designed to leave only one coordination site available as Lewis acids, new heptanuclear complexes such as $[Cr\{CN-Cu(tren)\}_6]^{9+}$ ($CrCu_6$) $[Cr\{CN-Ni(tetren)\}_6]^{9+}$ ($CrNi_6$) and $[Cr\{CN-Mn(tetren)\}_6]^{9+}$ ($CrMn_6$) have been synthesised and characterised (see Part 1[7]). Despite the high-spin value of these compounds ($S = 9/2$, 15/2, and 27/2, respectively), no single-molecule magnet behaviour has been observed, because their high symmetry leads to a uniaxial anisotropy D equal to zero. Thus, it was necessary to develop new synthetic routes to obtain polynuclear complexes with an effective control of the nuclearity and the structural anisotropy, one of the important parameters to understand and to tune.

There are very few examples of polynuclear complexes based on hexacyanometalate precursors in the literature. In addition to the heptanuclear complexes that are prevalently reported,[7, 10, 11, 16–19] only a few other species have been previously reported[20–22] and most of them have been obtained without effective control of the nuclearity.

Starting with a hexacyanometalate precursor, nine different polynuclear complexes with various geometries might be obtained, which are associated with the corresponding pseudo symmetry: dinuclear ($D_{\infty h}$), trinuclear–*cis* (C_{2v}), trinuclear–*trans* ($D_{\infty h}$), tetranuclear–*fac* (C_{3v}), tetranuclear–*mer* (C_{2v}), pentanuclear–*cis* (C_{2v}), pentanuclear–*trans* (D_{4h}), hexanuclear (C_{4v}) and heptanuclear (O_h) complexes (Figure 1). Modifying synthetic parameters, it has been possible to synthesise seven of them: di-, tri- tetra-, hexa- and heptanuclear, which are described in the present paper. We then illustrate the possibility of tuning the nuclearity of the target products and the potentiality of the strategy.

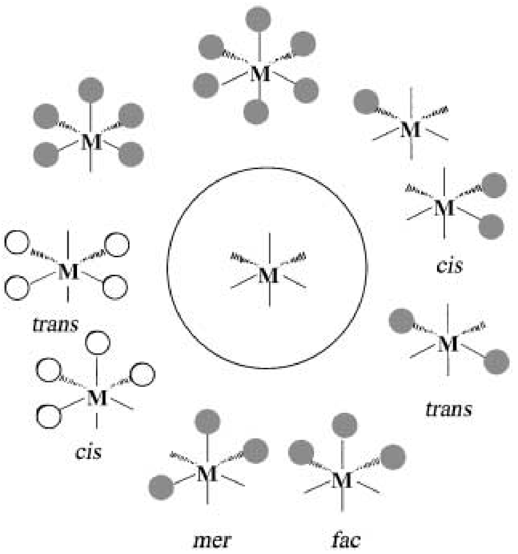


Figure 1. Schematic representation of the polynuclear complexes based on hexacyanometalate precursors: those described in the present publication are denoted by ● those not described by ○.

After presenting the synthetic route developed in this study, we shall discuss the experimental conditions that allow the formation of complexes of controlled nuclearity and then outline the main parameters involved in this investigation.

Synthetic strategy

The general synthetic method is the following: starting with a polydentate ligand (tetraamine for copper(II) and pentaamine for nickel(II)) and adding a metallic salt, it is possible to create a mononuclear precursor with one labile position available. The reaction of this mononuclear complex (Lewis acid) with hexacyanometalate precursors (Co^{III} or Cr^{III}) (Lewis base), allows the synthesis of polynuclear complexes. Following this strategy and by modifying the synthetic parameters such as the nature of the ligand, the counter anions and the stoichiometry, di-, tri-, tetra-, hexa- and heptanuclear complexes are selectively obtained:

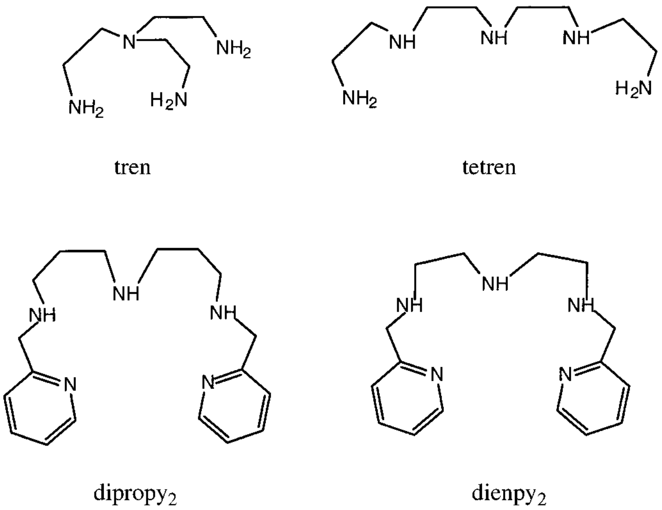
$$M'^{II} + L \rightarrow M'^{II}L \quad (1)$$

$$M'^{II}L + [M^{III}(CN)_6]^{3-} \rightarrow M'^{II}L + [M(CN)_5(CN-M'L)]^{-} \quad (2)$$

$$(n-1)M'^{II}L + [M(CN)_5(CN-M'L)]^{-} \rightarrow [M(CN)_{6-n}(CN-M'L)_n]^{(2n-3)+} \quad (3)$$

The formation of charged species is a key aspect of the synthetic strategy (see Part 1[7]). Highly charged complexes allow a good separation between the molecules in the solid state and the control of the intermolecular interactions, thanks to the use of different counterions. To avoid the precipitation of neutral products, we chose a trivalent core ($[M^{III}(CN)_6]^{3-}$) and divalent peripheral metallic cations (M'^{II}) bonded to neutral ligands L. Herein, only nickel(II) and copper(II) complexes surrounding hexacyanocobaltate(III) and hexacyanochromate(III) precursors are described. However, the strategy might be extended to other cations and different polyfunctionalised cores.[23]

Amine ligands and mononuclear complexes: Two commercially available polyamine molecules are employed in this study: the tetradentate tris(2-amino)ethylamine (tren) is used with copper(II), since it leads to stable complexes with trigonal geometry around the copper centre. The pentadentate tetraethylenepentamine ligand (tetren) is employed with nickel(II), since it gives stable complexes with octahedral symmetry around the nickel centre (in spite of the fact that it is known to adopt up to eight conformations).[24] Two other pentamine ligands[25, 26] are used: 1,9-bis(2-pyridyl)-2,5,8-triazanonane and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane, denoted as dienpy$_2$ and dipropy$_2$, respectively (Scheme 1). These polydentate pyridyl-containing ligands were prepared from diethylenetriamine or *N*-aminopropyl-1,3-propanediamine and 2-pyridinecarboxaldehyde, reactions that involved the one-to-two Schiff bases and subsequent hydrogenation with sodium borohydride.[27] The purity of the ligands was checked by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1. Ligands employed in this study.

After the synthesis of the ligands, the formation of the mononuclear complexes corresponds to the second step of the synthetic route. The ligands tetren, dienpy$_2$ and dipropy$_2$ are already known to form very stable complexes with nickel(II)[25, 26] and the stability constants K_{ML} are 2.5×10^{17} for $[Ni(tetren)(H_2O)]^{2+}$, 1.6×10^{19} for $[Ni(dienpy_2)(H_2O)]^{2+}$ and 2.4×10^{15} for $[Ni(dipropy_2)(H_2O)]^{2+}$.[25] The high stability of the complexes, which allows our strategy, is mainly due to the high basicity of the linear pentadentate tetren, to the π bonding between the pyridyl π or π^* and the t_{2g} orbitals of the metals and to the entropy gain associated with the formation of several chelate rings.

It is feasible to isolate these highly thermodynamically stable mononuclear complexes as single crystals and to use them as starting materials in the synthesis of polynuclear complexes. The mononuclear complexes $[Ni^{II}(tetren)(ClO_4)]^+$ (**1**) $[Ni^{II}(dienpy_2)(H_2O)]^{2+}$ (**2**) and $[Ni^{II}(dipropy_2)(H_2O)]^{2+}$ (**3**) are obtained by addition of an aqueous solution of nickel(II) tetrafluoroborate or perchlorate to a water–acetonitrile solution containing the polyamine ligand L (L = tetren, dienpy$_2$, dienpy$_2$). After a few days, crystals of the mononuclear nickel(II) complexes are isolated and used without further purification. For the copper(II) complexes, the formation of a trinuclear complex $[(tren)\{Cu^{II}(tren)\}_3]^{6+}$ (see Part 1[7]) does not allow isolation of the mononuclear species from tren and copper(II).

Polynuclear complexes: The hexacyanometalate precursors, $[Co^{III}(CN)_6]^{3-}$ or $[Cr^{III}(CN)_6]^{3-}$ are added to the mononuclear complexes, generated in situ or previously isolated as crystals. After slow evaporation of the solvent, the polynuclear complexes with the appropriate number of counter anions are isolated as crystals and characterised by several techniques including IR, X-ray crystallography and mass spectrometry.

The synthesis of the dinuclear complex, $[Cr(CN)_5\{CN{-}Ni(dienpy_2)\}]^-$, denoted as CrNi, has been performed with the precursors $[Cr(CN)_6]^{3-}$ and $[Ni(dienpy_2)(H_2O)]^{2+}$ in a stoichiometric amount, in the presence of the large cations tetraphenylphosphonium and tetraphenylarsonium. This favours the selective crystallisation of the large $[CrNi]^-$ ion, regardless of the nature of the ligand L around the nickel center. The resultant product is soluble in organic solvents such as dichloromethane, ethanol or acetonitrile. Similar experiments have been performed starting with a hexacyanocobaltate(III) precursor leading to similar CoNi species but the quality of the crystals were not suitable for single-crystal X-ray diffraction.

To obtain the *trans*-trinuclear complexes $[M(CN)_4(CN{-}M'(L))_2]^+$, MM'$_2$, two strategies might be used:

1) Using dienpy$_2$ as the ligand and tetrafluoroborate or perchlorate as the counter anion, in the presence of a hexacyanometalate, the trinuclear complexes are obtained selectively ($M = Co^{III}$, Cr^{III}; $M' = Ni^{II}$). Thus, the ligand induces the formation of the cobalt(III)- or chromium(III)-centred species $[Co^{III}(CN)_4\{CN{-}Ni(dienpy_2)\}_2](BF_4)$ and $[Co^{III}(CN)_4\{CN{-}Ni(dienpy_2)\}_2](ClO_4)$, denoted as CoNi$_2$(dienpy$_2$), $[Cr^{III}(CN)_4\{CN{-}Ni(dienpy_2)\}_2](BF_4)$ and $[Cr^{III}(CN)_4\{CN{-}Ni(dienpy_2)\}_2](ClO_4)$, denoted as CrNi$_2$(dienpy$_2$). All the CrNi$_2$ compounds are described in Part 3.[9] In this way, the formation of the *trans*-trinuclear complex might be explained by the steric effect induced by the bulky ligand and by the presence of the two pyridyl rings in *trans* positions as indicated by X-ray crystallography.
2) The second way to obtain *trans*-trinuclear complexes is to use smaller ligands, tetren for example, and a specific counter anion, such as chloride. Thus, starting with a nickel(II) chloride precursor, in the presence of tetren, it was possible to selectively obtain the *trans*-trinuclear complex, $[Co(CN)_4\{CN{-}Ni(tetren)\}_2]Cl$, denoted CoNi$_2$(tetren).

The *cis*-trinuclear and the *mer*-tetranuclear complexes have been obtained as co-crystallised species in the synthesis of Co–Cu complexes. The reaction was performed in water–

acetonitrile solution by addition of the tren ligand to a copper perchlorate, which led to the formation of the mononuclear complex in situ, before the $[Co(CN)_6]^{3-}$ precursor was added. In this reaction the stoichiometry plays an important role and the Cu/Co ratio must be smaller than 4:1 to avoid the formation of the heptanuclear $CoCu_6$ complex. The difference between the copper(II) and the nickel(II) complex in the formation *cis/trans* or *fac/mer* polynuclear complexes is discussed below.

The *fac*-tetranuclear complexes were obtained by using the $dipropy_2$ ligand in the presence of tetrafluoroborate or perchlorate salts and, once again, the ligand influences the formation of an isostructural *fac* family. The reaction was performed in a water–acetonitrile solution of the isolated mononuclear Ni^{II} complex by addition of the hexacyanometalate. In this way, for example, the $[Co^{III}(CN)_3(CN{-}Ni(dipropy_2))_3](BF_4)_3$ complex, denoted $CoNi_3$, was synthesised and fully characterised.

No pentanuclear complexes were obtained starting with hexacyanometalate precursors despite the attempts performed with specially designed ligands. Specific attention was paid to the synthesis of $[Co^{III}(CN)_2\{CN{-}Cu(tren)\}_4](ClO_4)_5$, a $CoCu_4$ complex that might exist considering that the $FeCu_4^{III}$ analogue has been reported.[18] Despite our endeavors, until now we have not isolated single crystals suitable for X-ray crystallography.

The hexanuclear complex $CoNi_5$ was obtained without effective control of the nuclearity. Initially, we thought that the stoichiometry played an important role in the synthesis and used a 5:1 Ni:Co ratio. However, it appears that the hexanuclear complex $CoNi_5$ crystallises as the thermodynamically stable product when using pure tren ligand, regardless of the initial Ni:Co stoichiometric ratio (from 1:3 to 1:7).

The heptanuclear complexes were prepared with Ni^{II}–tetren and Cu^{II}–tren as precursors and perchlorate salts as counter anions in water–acetonitrile mixtures. In this way, $CrNi_6$, $CoNi_6$, $CrCu_6$ and $CoCu_6$ were obtained and characterised (see Part 1[7]).

These results demonstrate clearly the importance of the synthetic parameters in controlling and tuning the nuclearity of the polynuclear compounds and some of the unavoidable limits. We now focus on the three main factors to master: the nature of the counter anions, the nature of the ligands and the stoichiometry.

Counter anions: The choice of the counterion is important and allows the crystallisation of specific compounds. Thus, using the same ligand under similar experimental conditions (same solvent, metallic ion and concentrations), the final products differ according to the nature of the salt. For example, a nickel(II) perchlorate, in the presence of the tetren ligand and hexacyanochromate(III) precursors, leads to the heptanuclear complex $CrNi_6$, whereas $CrNi_2$ is obtained when using the nickel(II) chloride. The thermodynamic stability of the chloro derivative of the trinuclear complex undoubtedly explains such a result. Similarly, the synthesis of heterodinuclear complexes takes advantage of the negative charge of the final product. Regardless of the nature of the polyamine, the reaction between a trivalent hexacyanometalate $[M^{III}(CN)_6]$ and a divalent peripheral metallic cation (M′) in the presence of large cations, such as $AsPh_4$ or PPh_4, favours the dinuclear species: in aqueous solution, the association of loosely solvated large cations and large anions leads to weak solubility constants and to precipitation. Thus the reaction of the $[Cr(CN)_6]^{3-}$ precursor and of the mononuclear $[Ni(L)]^{2+}$ complex, in the presence of tetraphenylarsonium, leads to thin crystalline plates of $[AsPh_4]^+[CrNi]^-$ containing the dinuclear $[CrNi]^-$ ion.

Reaction of an excess of the mononuclear nickel(II) precursor with hexacyanometalate in the absence of the $AsPh_4$ or PPh_4 cations leads to higher nuclearity highly charged cations $[CrNi_n]^{(2n-3)+}$.

Polyamine ligands: According to the nature of the polyamine, tri-, tetra- or heptanuclear complexes crystallise. Several experiments were performed with three different ligands: tetren, $dienpy_2$ and $dipropy_2$. The resulting products differ from each other with regard to the steric hindrance exhibited and to the conformation of the ligand surrounding the nickel ion. The tetren ligand is used successfully in the formation of the $CrNi_6$ heptanuclear complex (see Part 1[7]). Under similar experimental conditions, the ligand $dienpy_2$ leads to trinuclear complexes, whereas $dipropy_2$ leads to tetranuclear entities. Regardless of the nature of the hexacyanometalate core ($[Cr^{III}(CN)_6]$ or $[Co^{III}(CN)_6]$), of the peripheral cation [Ni^{II} or Cu^{II}] or of the counter anion (tetrafluoroborate or perchlorate), the final products are isonuclear: $CoNi_2$ and $CrNi_2$ for the $dienpy_2$ series, and $CoNi_3$ and $CrNi_3$ for the $dipropy_2$ family. In such a case, the nuclearity is clearly induced by the ligand itself. The result can be extended to other metallic ions.

Stoichiometry: The stoichiometry also plays an important role, especially in syntheses with the copper complexes. It was demonstrated that when an excess of a mononuclear Cu^{II} complex was used in the presence of hexacyanocobaltate(III), the final product was the heptanuclear complex $CoCu_6$ with or without the co-crystallised trimer (see Part 1[7]). With a smaller $Cu{:}M(CN)_6$ ratio (1:4), $CoCu_2$ and $CoCu_3$ complexes were obtained.

The *trans*-trinuclear complexes with peripheral nickel(II) are particularly stable. Nine different crystallographic structures were obtained, and two of them are described herein. Several factors explain why the trinuclear complexes are preferentially formed and why the *trans* configuration is favoured, after the first step leading in solution to the dinuclear $[M^{III}(CN)_5CN{-}M'^{III}L)]^-$ or $[MM'L]^-$: Firstly, simple electrostatics allows us to understand the preferred formation of the trinuclear complex: the cationic $M'L^{2+}$ complex is attracted by the anionic $[MM'L]^-$ unit to form the trinuclear $[M(M'L)_2]^+$ ion, while it is repelled by the $[M(M'L)_2]^+$ ion to form the tetranuclear $[M(M'L)_3]^{3+}$ ion. Secondly, the *trans* approach of the cationic $M'L^{2+}$ to $[MM'L]^-$ is favoured compared to the *cis* one since the steric hindrance induced by the ligand L and the local electrostatic repulsions are stronger in the *cis* positions than in the *trans* one. Thirdly, the electronic density, delocalised over the peripheral nitrogen atoms of the dinuclear species $[MM'L]^-$ (that is, the basic character) influences the interaction with the approaching ML^{2+}. Hückel calculations performed on a dinuclear $[MM'L]^-$ model (with $M = Cr$, $M' = Ni$, $L = NH_3$), indicate that the nitrogen atom of the cyano group in the *trans* position of the attached M′L bears a more negative charge than the *cis* ones. Instead, similar calculations for a dinuclear $[CrCu]^+$ model complex suggest that the nitrogen atom of the *cis* cyanides is more negative than the *trans* one, which may explain a) the preferred formation of *trans*-trinuclear nickel(II) $[M(NiL)_2]^+$ complexes and the possibility to obtain *cis*-trinuclear copper(II) $[M(CuL)_2]^+$ complexes and even b) the formation of the *mer*-tetranuclear $CoCu_3$ complex. Fourthly, more difficult to rationalise is the formation of the tetranuclear complex with the *fac* geometry. More accurate calculations are required in which the full ligand geometry is used to determine more precisely the basicity of the nitrogen atoms (aliphatic amine or pyridine) and its influence on long distance effects.

Infrared spectroscopy: The complexes CrNi, CoNi, $CoNi_2$(tetren), $CoNi_2(dienpy_2)$, $CoNi_3$, $CoNi_5$ and $CoNi_6$ were characterised by their IR spectra. For all species, except for the monoanionic $[CrNi]^-$ and $[CoNi]^-$ complexes, the distinctive bands of the perchlorate or tetrafluoroborate counter anions (1090 and 1085 cm^{-1}, respectively) clearly indicate the presence of positively charged complexes. The intensity of the bands increases as the total charge of the final product varies from one (trinuclear), three (tetranuclear), seven (hexanuclear) up to nine counter anions for the heptanuclear complexes. The presence of bands of the tetraphenylarsonium (at 452, 690, 750, 997 and 1079 cm^{-1}) confirms the negative charge of the $[CrNi]^-$ and $[CoNi]^-$ units.

In the frequency range for asymmetric stretches of cyanide, 2200–2000 cm^{-1}, several bands are observed, the number of which is dependent on the coordination type of the bidentate CN ligand. Vibrations of free and bridged cyanides are noticeable in the spectrum and can be compared to the ones of free hexacyanochromate(III) and hexacyanocobaltate(III) precursors (2131 and 2130 cm^{-1}, respectively). CrNi exhibits a weak band at 2151 cm^{-1}, which is related to the bridging cyanide, and stronger ones at 2120 and 2129 cm^{-1}, which are attributed to the free cyanide. The difference between the different terminal CN stretching bands might be due to hydrogen bonding in the crystal or to *cis*- and *trans*-cyanide. Similar bands are observed for the CoNi (2119, 2128, 2157 cm^{-1}), $CoNi_2$(tetren) (2117, 2131, 2142 cm^{-1}), $CoNi_2(dienpy_2)$ (2136, 2141(sh) cm^{-1}), $CoNi_3$ (2141 and 2170 cm^{-1}) and $CoNi_5$ (2135(sh), 2156 cm^{-1}) complexes, for which the intensity increases with an increasing number of bridging cyanides. Only one single band at 2152 cm^{-1} is visible in the $CoNi_6$ spectrum, where all the cyano groups are bridging. The CN stretching bands are summarized in Table 3. In the series of CoNi complexes, the wavenumber of the bridging CN stretching band increases, up to 2170 cm^{-1} depending on the structural and electronic characteristics of the bonding cyanide. The stretching value is related to the C-N-Ni angle, which differs from one complex to another (see Part 1[7]). Table 4 and Figure 2, which displays the ν_{CN} band versus the distortion of the C-N-Ni entity in hexacyanocobaltate(III)-centred nickel(II) complexes, show the direct correlation between the energy of the stretching band of the bridging cyanide (2138–2170 cm^{-1}) and the C-N-Ni angle (145–174°). Similar observations are valid for hexacyanochromate(III)-centred nickel complexes (Part 3[9]).

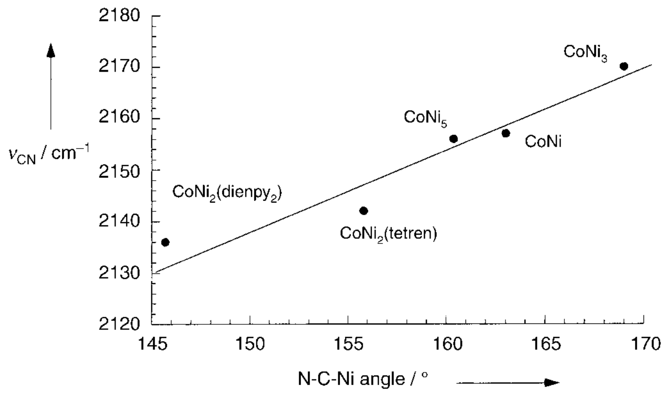


Figure 2. Plot of the stretching bands ν_{CN} versus the distortion of the C-N-Ni bridge.

Structural study: Single-crystal X-ray diffraction is a useful technique for the present study because it allows the characterization of the polynuclear nature of the complexes as well as the structural parameters (bond lengths, angles, packing, intermolecular distances) that influence the magnetic properties.

The bi-, tri- (*cis* and *trans*), tetra- (*fac* and *mer*), hexa- and heptanuclear complexes, as well as the nickel(II) mononuclear complexes were characterised by X-ray crystallography. The principal crystallographic data are summarized in Tables 1 and 2. In all cases, $[Ni(tetren)(ClO_4)](ClO_4)$ (**1**), $[Ni(dienpy_2)(H_2O)](ClO_4)_2$ (**2**), $[Ni(dipropy_2)(H_2O)](BF_4)_2$ (**3**), and in CrNi, $CoNi_2$(tetren), $CoNi_2(dienpy_2)$, $CoNi_3$, $CoNi_5$ and $CrNi_6$, the mononuclear or the polynuclear entities $[M(CN)_{6-x}(CN{-}M'L)_x]^{n+}$ are well defined without disorder on the polyamine ligand.

Surprisingly, there are only a few examples in the literature of crystallographic mononuclear nickel complexes chelated by a linear pentadentate polyamine ligand. To our knowledge, with regard to the pentadentate tetren, $dipropy_2$ and $dienpy_2$ ligands, only cobalt complexes have been characterised by X-ray crystallography,[28–30] even though the nickel species have already been described and commonly used in the formation of polynuclear complexes. The compounds **1**–**3** are of great interest in the step-by-step synthetic strategy discussed in the present paper. They comprise the pentadentate ligand, which blocks five of the six coordination sites of the nickel(II), the last position is occupied by a counter anion or a water molecule. These compounds might serve as precursors in the formation of new polynuclear complexes.

The complex $[Ni(tetren)(ClO_4)](ClO_4)$ (**1**; Figure 3a) was isolated as purple hexagonal crystals. The crystallographic data indicate an orthorhombic system and a *Pbca* space group with the following cell parameters: $a = 13.862(4)$, $b = 15.747(8)$, $c = 31.984(14)$ Å. Two different nickel atoms are present in the asymmetric unit. Among the eight different conformations that might exist with tetren, two are present in the unit cell, corresponding to the two different diaster-

Table 1. Crystallographic data of the mononuclear complexes **1**–**3**.

	1 $[Ni(tetren)(ClO_4)](ClO_4)$	**2** $[Ni(dienpy_2)(H_2O)](ClO_4)_2$	**3** $[Ni(dipropy_2)(H_2O)](BF_4)_2$
chemical formula	$C_8H_{23}Cl_2N_5Ni_2O_8$	$C_{16}H_{27}Cl_2N_5NiO_{10}$	$C_{18}H_{29}B_2F_8N_5NiO$
*F*w	446.92	579.03	563.78
crystal system	orthorhombic	monoclinic	monoclinic
a [Å]	13.862(4)	8.548(3)	17.764(7)
b [Å]	15.747(8)	10.797(3)	8.252(8)
c [Å]	31.984(14)	26.753(7)	18.417(4)
α [°]	90	90	90
β [°]	90	93.01(3)	117.93(3)
γ [°]	90	90	90
V [Å^3]	6962(5)	2466(1)	2385(1)
Z	16	4	4
space group	*Pbca*	$P2_1/n$	*Cc*
crystal shape	parallelepiped	parallelepiped	parallelepiped
crystal colour	violet	violet	blue
data collected	6772	4913	2336
unique data collected		4315	2096
data used for refinement	2823 $(F_o)^2 > 3\sigma\ (F_o)^2$	2937 $(F_o)^2 > 3\sigma\ (F_o)^2$	1902 $(F_o)^2 > 2\sigma\ (F_o)^2$
$R^{[a]}$	0.0508	0.0697	0.0310
$R_w^{[b]}$	0.0570	0.0818	0.0371
variables	384	309	344
$\Delta\rho_{min}$ [e Å^{-3}]	−1.42	−0.42	−0.32
$\Delta\rho_{max}$ [e Å^{-3}]	0.96	0.65	0.35

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

Table 2. Crystallographic data for the polynuclear complexes CrNi, $CoNi_2$(tetren), $CoNi_2(dienpy_2)$, and $CoNi_3$.

	CrNi $[Cr(CN)_5\{CNNi(dienpy_2)\}]_2$ $(As(C_6H_5)_4)_2$, 6 H_2O	$CoNi_2$(tetren) $[Co(CN)_4\{CNNi(tetren)_2\}]$ Cl, 7 H_2O	$CoNi_2(dienpy_2)$ $[Co(CN)_4\{CNNi(dienpy_2)_2\}]$ (BF_4), 9 H_2O	$CoNi_3$ $[Co(CN)_3\{CNNi(dipropy_2)_3\}]$ $(BF_4)_3$, 6 H_2O
chemical formula	$C_{92}H_{98}As_2Cr_2N_{22}Ni_2O_6$	$C_{22}H_{60}ClCoN_{16}Ni_2O_7$	$C_{38}H_{64}BCoF_4N_{16}Ni_2O_9$	$C_{60}H_{93}B_3CoF_{12}N_{21}Ni_3O_6$
*F*w	3958.37	872.6	1152.18	1699.99
crystal system	triclinic	monoclinic	monoclinic	trigonal
a [Å]	12.7971(10)	14.378(2)	34.977(18)	18.343(22)
b [Å]	17.7015(13)	8.420(1)	10.389(2)	18.343(15)
c [Å]	23.2455(17)	16.518(2)	14.987(9)	23.394(18)
α [°]	109.796(2)	90	90	90
β [°]	98.546(2)	98.88(1)	109.35(5)	90
γ [°]	96.042(2)	90	90	120
V [Å^3]	4830.6(6)	1975.6(6)	5138(5)	6818(12)
Z	2	2	2	3
space group	$P\bar{1}$	$P2_1/c$	*C*2/*c*	*R*3
crystal shape	thin plates	hexagonal plates	parallelepiped	cube
crystal colour	pink	violet	pink	pink
data collected	17504	6323	5545	2944
unique data collected	11844	5734	5040	2669
data used for refinement	11844	3827 $(Fo)^2 > 3\sigma\ (Fo)^2$	2879 $(F_o)^2 > 3\sigma\ (F_o)^2$	1203 $(F_o)^2 > 3\sigma\ (F_o)^2$
R	0.1434	0.0402	0.056	0.0955
R_w	0.2662	0.0444	0.07	0.1103
variables	535	309	296	151
$\Delta\rho_{min}$ [e Å^{-3}]	−0.553	−0.50	−0.468	−0.53
$\Delta\rho$max [e Å^{-3}]	1.441	0.37	0.863	0.69

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w|F_o| - |F_c|^2/\Sigma w F_o^2]^{1/2}$.

eoisomers. The tetren ligand is bound to the nickel(II) centre by five nitrogen atoms (Ni–N mean distance 2.095 Å). The position left available on the nickel(II) ion by the pentadentate ligand is occupied by a perchlorate anion. The Ni–O distance is 2.30(1) Å, similar to that in other perchlorate–nickel compounds when the counter anion is present in the first coordination sphere.[31, 32] The transition-metal ion resides in an octahedral environment, which is elongated along the Ni–O direction; the *cis* N-Ni-N angles vary from 83 to 101°. Similar twisting is observed for the *trans* N-Ni-N angle with values ranging from 166 to 174°.

The complex $[Ni(dienpy_2)(H_2O)](ClO_4)_2$ (**2**; Figure 3 b) was isolated as violet parallelepiped crystals (monoclinic system, *P*21/*n* space group, *a* = 8.548(3), *b* = 10.797(3), *c* = 26.7537(7) Å, *β* = 93.01(3)°). There is an octahedral arrangement around the nickel centre with five Ni–N bonds (mean distances 2.08 Å) and one Ni–O bond (2.135 Å, for the water molecule). The two pyridine rings are oriented *cis* to each

Table 3. Selected interatomic distances [Å] and angles [°] in the complexes CrNi, CoNi$_2$(tetren), CoNi$_2$(dienpy$_2$), and CoNi$_3$.

	CrNi	CoNi$_2$(tetren)	CoNi$_2$(dienpy$_2$)	CoNi$_3$
interatomic distances [Å]				
C–N bridge	1.15(3)	1.152(3)	1.143(6)	1.14(2)
C–N free	1.20, 1.18, 1.18 1.10, 1.20	1.145(3), 1.139(3)	1.140(7)	1.13(3)
Cr (or Co)–CN bridge	2.05(3)	1.894(2)	1.882(4)	1.87(2)
Cr (or Co)–CN free	1.95, 2.01, 2.03, 2.04, 2.06	1.901, 1.896	1.901(5), 1.898(5)	1.91(2)
M–CN	2.13(3)	2.125(2)	2.115(4)	2.03(2)
M–N11	1.97(3)	2.127(3)	2.112(4)	2.099(17)
M–N12	2.08(2)	2.080(2)	2.124(4)	2.11(2)
M–N13	2.14(2)	2.112(2)	2.076(4)	2.13(2)
M–N14	2.17(2)	2.114(2)	2.082(4)	2.08(2)
M–N15	2.17(2)	2.112(2)	2.062(4)	2.13(3)
bond angles [°]				
Cr (or Co)–CN bridge	173.3(3)	173.3(2)	172.4(4)	177.6(20)
Cr (or Co)–CN free	171, 176, 177, 173, 165	178.1(2), 177.2(3)	177.2(5), 179.2(5)	178.2(22)
CN–M cyanide	163.2	155.8(2)	145.8(4)	169.0(19)
N11-M-cyanide	82.4	85.58(9)	89.2(2)	174.2(8)
N12-M-cyanide	90.2	92.30(9)	170.5(2)	92.7(8)
N13-M-cyanide	92.3	94.19(9)	90.1(2)	90.3(8)
N14-M-cyanide	91.3	172.15(9)	93.7(2)	88.8(9)
N15-M-cyanide	171.3	91.46(9)	91.2(2)	93.2(9)

Table 4. Best fit values for parameters J, g, D and zJ' for the complexes CrNi, CoNi, CoNi$_2$(tetren), CoNi$_2$(dienpy$_2$), CoNi$_3$, CoNi$_5$ and CoNi$_6$.

	IR: ν_{CN} bridge) [cm^{-1}]	IR: ν_{CN} free [cm^{-1}]	θ, C-N-Ni [°]	$J_{exp.}$	g	zJ'	D	R
CrNi	2151	2120, 2129	163.2	18.5	1.98	− 0.144	− 0.16	1×10^{-4}
CoNi	2157	2119, 2128		–	–	–	–	–
CoNi$_2$(tetren)	2142	2117 & 2131	155.8	− 0.13	2.02	–	–	1×10^{-5}
CoNi$_2$(dienpy$_2$)	2138	2136	145.8	− 0.10	2.04			3×10^{-3}
CoNi$_3$	2172	2141	169	− 0.43	1.95			8×10^{-4}
CoNi$_5$	2156	2142	158.4, 159.1, 158.6, 157.0, 174.9 (*trans*)	− 0.15	2.02			2×10^{-3}
CoNi$_6$	2152	–	–	− 0.45	2.0	− 0.005		1.6×10^{-3}

other and to the water molecule. The *cis* N-Ni-N angles (between 80 to 101°) and the *trans* N-Ni-N angles (163 and 176°) indicate the high distortion of the octahedral environment of the nickel ion.

The complex [Ni(dipropy$_2$)(H$_2$O)](BF$_4$)$_2$ (**3**; Figure 3c) forms dark blue parallelepiped crystals (monoclinic system, *Cc* space group, with the following cell parameters: $a = 17.764(7)$, $b = 8.252(8)$, $c = 18.417(4)$ Å, $\beta = 117.93(3)$ Å). One mononuclear complex is present in the asymmetric unit as well as two tetafluoroborate anions that compensate the cationic charge. The nickel ion resides in a quasi-octahedral environment and, as expected, the polyamine ligand chelates five of the six coordination sites leaving one position occupied by a water molecule: five Ni–N bonds (mean distances 2.115 Å), one Ni–O bond (2.142 Å), *cis* N-Ni-N angles (between 81.30 to 97.17°), *trans* N-Ni-N angles (169.5 and 174.0°). The conformation of the dipropy$_2$ ligand is well defined, with no disorder of the carbon atoms of the ligand. The two pyridine rings are oriented *cis* to each other, one of them being oriented *trans* to the water molecule.

The conformation of the ligands induced a chiral structure. In contrast to **1** and **2**, in **3** the non-centrosymmetric space group (*Cc*) indicates that the two enantiomers are not present in the unit cell of a same crystal, but exist separately in different crystals. Chirality is also present in other complexes such as CoNi$_3$. This topic will be discussed in detail together with a description of the enantiomeric separation, the absolute configuration, dichroism, in a future publication.

The CrNi complex (Figure 4) crystallises as very thin and fragile pink plates of the tetraphenylarsonium salt (for the parameters, see Table 2). Three heavy atoms are present in the asymmetric unit: the chromium, nickel, and arsenic atoms. The latter is surrounded by four phenyl fragments of the tetraphenylarsonium cation that plays the role of the counter cation to balance the anionic charge of the heterometallic dimer. In the CrNi dinuclear unit, the hexacyanochromate(III) fragment is slightly distorted compared to the potassium salt (mean Cr–C distances 2.05 Å; mean C–N distances 1.13 Å). One CN ligand bridges the unique nickel ion present in the unit cell. The C–N distance is in the range of values published for cyano bridges[33] and in the other structures reported herein. The C-N-Ni angle deviates moderately from linearity (163.02°; Table 3). The conformation of the dienpy$_2$ ligand (the two pyridine rings are oriented *cis* to each other and to the cyano bridge) is the same as that observed in the mononuclear and trinuclear complexes. The packing is formed by layers of dinuclear species separated by AsPh$_4^+$ ions; the interlayer distance is 9 Å.

The CoNi$_2$(tetren) complex (Figure 5), which is obtained as violet hexagonal plates, crystallises in the monoclinic system in the $P2_1/c$ space group (Table 2). The asymmetric unit contains two heavy atoms (one cobalt atom is located on

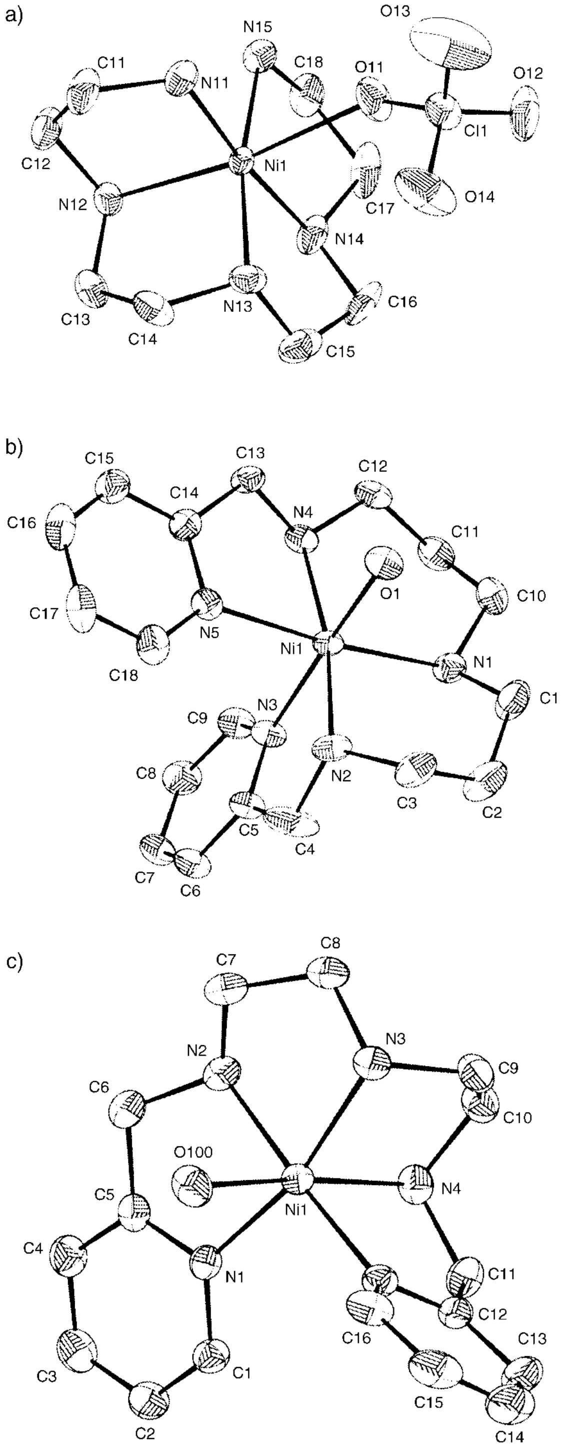


Figure 3. X-ray crystal structure of the cations in the mononuclear nickel complexes **1** (a), **2** (b), and **3** (c).

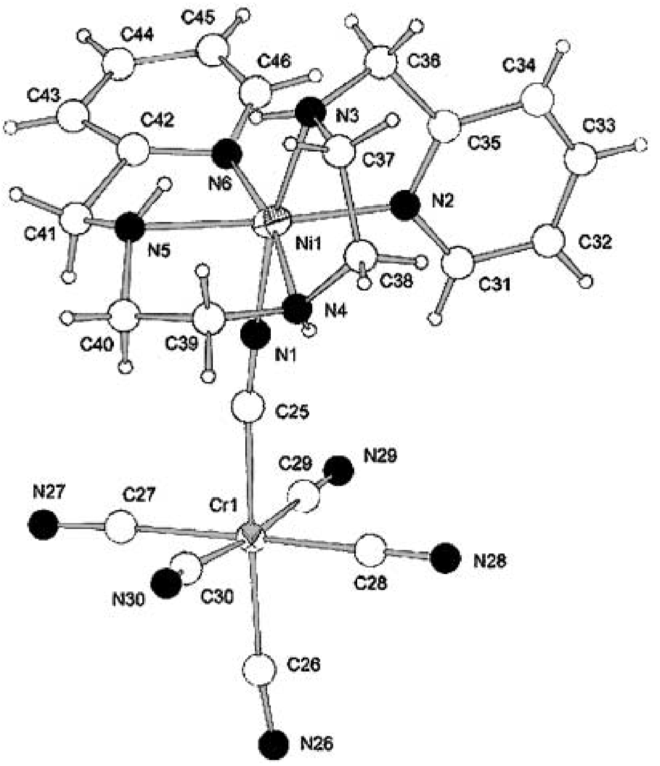


Figure 4. X-ray crystal structure of the [tren{Cu(tren)$_3$}]$^{6+}$ entity in CrNi.

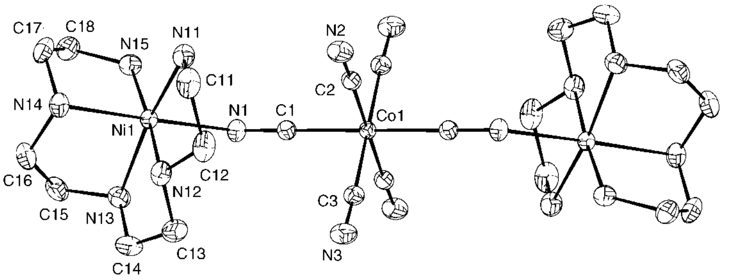


Figure 5. X-ray crystal structure of the [Cr(CN)$_4${CN–Ni(tetren)}$_2$]$^+$ entity in CoNi$_2$-tetren.

an inversion centre and one nickel atom is in a general position) and a chloride ion (as counter anion). In the CoNi$_2$ trinuclear unit, the hexacyanocobaltate(III) fragment is slightly distorted compared to the potassium salt (mean Co–C distances 1.897 Å, mean CN distances 1.145 Å). Four unbonded cyanides with Co-C-N angles close to linearity (178.1(2) and 177.2(3)°) lie in equatorial positions of the complex. In axial positions, the cobalt(III) centre is linked to two nickel ions through CN bridges, which leads to a *trans*-trinuclearcomplex with a N–Ni distance of 2.112(2) Å, and Co-C-N and C-N-Ni angles of 173.3(2) and 155.8(2)°, respectively. The tetren ligand occupies the other five coordination sites of the nickel centre, which adopts a distorted octahedral symmetry. The distances and angles of the cyano bridges are given in Table 3. Seven water molecules per unit cell build a network of hydrogen bonds. The CoNi$_2$ molecules pack in such a way that all the molecules lie in the same direction. A detailed report of the packing in these complexes is given in Part 3[9] together with the description of four different CrNi$_2$ complexes.

The second *trans*-trinuclear complex obtained, CoNi$_2$(dienpy$_2$) (Figure 6), is formed with a dienpy$_2$ ligand coordinated to the nickel centre and tetrafluoroborate as counter anions. The product forms pink parallelepiped crystals (monoclinic, space group *C*2/*c*, for the parameters see Table 2), isostructural with perchlorato equivalent complexes formed with perchlorate

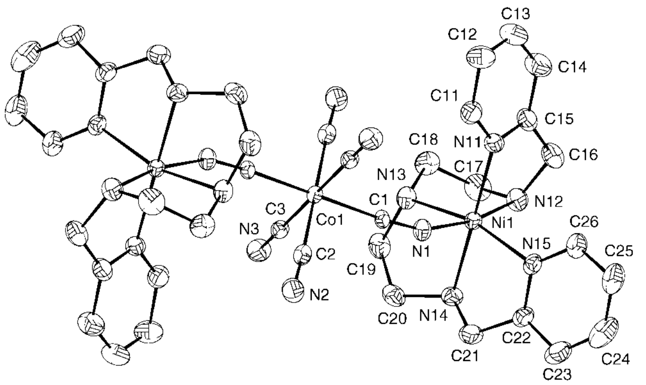


Figure 6. X-ray crystal structure of the $[Co(CN)_4\{CN{-}Ni(dienpy_2)\}_2]^+$ entity in $CoNi_2(dienpy_2)$.

salt and/or other metallic transition metals under similar experimental conditions. Two metallic atoms (one chromium and one nickel) are present in the asymmetric unit. The presence of an inversion centre on the chromium ion generates the trinuclear complex. The boron atom of the tetrafluoroborate anions is also on a specific position that generates the complete tetrahedral structure from two fluoride atoms. The unique positive charge of the trinuclear complex is then compensated by one BF_4^- ion. The cobalt centre is close to octahedral with *cis* and *trans* C-Co-C angles close to 90 and 180°, respectively. The Co–C bond lengths are in accordance with the literature values in related compounds[33, 34] (mean Co–C distances 1.894 Å, mean C–N distances 1.143 Å). The nickel atom in the $[Ni(dienpy_2)]^{2+}$ unit adopts a distorted octahedral geometry with significant variations of the Ni–N bonds (from 2.063(4) to 2.120(4) Å) and the *cis* N-Ni-N angles range from 81.3(2) to 101.88(19)°, whereas the *trans* N-Ni-N angles vary from 163.78(19) to 174.85(19)°. The axial Co-CN-Ni bridge appears very distorted with Co-C-N and C-N-Ni angles of 172.4(4) and 145.7(4)°, respectively. Despite this axial strong distortion, the other equatorial CN groups are close to linearity (179.5(5) and 177.2(5)°). The conformation of the $dienpy_2$ ligand is the same as in the mononuclear Ni complex and in the CrNi structure. In the unit cell, the molecules are well ordered in the *ac* plane, forming columns separated by BF_4^- ions. The distance between two adjacent layers is approximately 3 Å, whereas the shortest Co–Ni intermolecular distance is 6.8 Å (compared to 4.8 Å for the intramolecular ones).

The trinuclear *cis* and the tetranuclear *mer* complexes, $CoCu_2$ and $CoCu_3$ (Figure 7) co-crystallised, as blue parallelepipeds, in a 1:1 ratio. The poor quality of the X-ray structure does not allow a complete description of the structure (bond, distances). Nevertheless, the two products have been identified without ambiguity and are included here to demonstrate the feasibility of the formation of this kind of geometry.

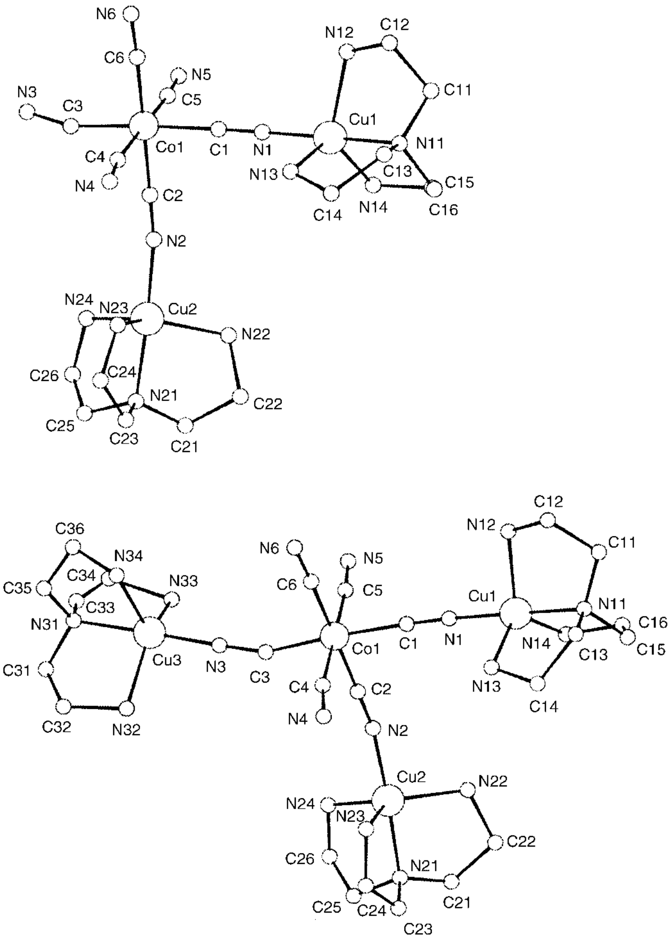


Figure 7. X-ray crystal structure of the $[Co(CN)_4\{CN{-}Cu(tren)\}_2]^+$ (top) and $[Co(CN)_3\{CN{-}Cu(tren)\}_3]^{3+}$ entities (bottom) in $CoCu_2{-}CoCu_3$.

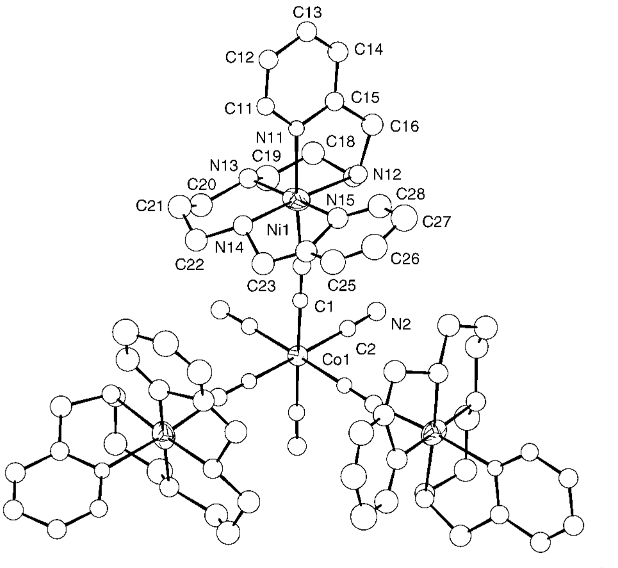


Figure 8. X-ray crystal structure of the $[Co(CN)_3\{CN{-}Ni(dipropy_2)\}_3]^{3+}$ entity in $CoNi_3$.

The tetranuclear *fac* $CoNi_3$ complex (Figure 8), which crystallises as pink cubes, is formed with the $dipropy_2$ ligand as the tetrafluoroborate salt. The compound crystallises in the trigonal system, space group *R*3 (Table 2). Only two metal ions (cobalt and nickel) are present in the asymmetric unit: the cobalt ion is on the C_3 axis, bound to two crystallographically different cyano groups, and the nickel atoms are in a general position, surrounded by the $dipropy_2$ ligand. Then the C_3 axis induces the *fac* tetranuclear complex. In addition, a BF_4^- ion, located on a general position, generates the three tetrafluoroborate anions necessary to compensate the charge of the polynuclear complex. Once again, the hexacyanocobaltate(III) core is close to the ideal octahedral symmetry with Co–C bonds of 1.87(2) and 1.91(2) Å, the *cis* C-Co-C angles near 90° and the *trans* C-Co-C angles close to 180°. The C–N bonds are 1.14(2) and 1.13(3) Å. The nickel atom resides in a distorted octahedral environment. The C-N-Ni angle slightly deviates from linearity (169°). The packing is of particular interest because the molecular anisotropy induced by the *fac* configuration is maintained in the unit cell, the molecular C_3 axis becoming a crystal anisotropy axis.

The $CoNi_5$ complex (Figure 9), which formed with the tetren ligand as a perchlorate salt, crystallises in the monoclinic system, space group $P2_1$ (for the parameters, see Experimental Section). Despite the low symmetry, the presence of two individual $[Co(CN)\{CN{-}Ni(tetren)\}_5]^{7+}$ entities in the asymmetric unit, and the presence of the expected 14 perchlorate anions (for a total of 236 atoms without counting the hydrogen atoms), the crystallographic structure was fully determined. Only five nickel atoms are bonded to the cyanides around the distorted octahedral hexacyanocobaltate(III) unit. The quality of the X-ray structure is not sufficient to give precise distances and angles.

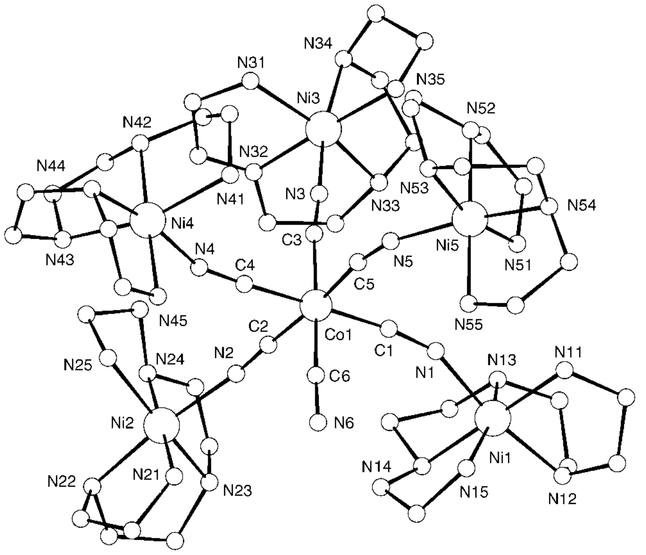


Figure 9. X-ray crystal structure of the $[Co(CN)\{CN{-}Ni(dipropy_2)\}_5]^{7+}$ entity in $CoNi_5$.

The crystallographic structure of the $CrNi_6$ (trigonal, $R\bar{3}$) was described in Part 1[7] of this series. Only cell parameters were obtained for the $CoNi_6$ complex.

Mass spectrometry: Electrospray the mass spectrometry was used to characterise these highly charged complexes, and the results obtained are in agreement with the expected structures. Moreover, the technique allows the characterisation of the nuclearity of the complexes and the study of their thermodynamic stability in solution. The only two anionic species, CrNi and CoNi, were detected by using the negative-ion mode, and the corresponding molecular peaks were observed at *m*/*z* 1013.5 and 1017 and are attributed to $[Cr(CN)_5\{CN{-}Ni(dienpy_2)\}]^-$ and $[Co(CN)_5\{CN{-}Ni(dienpy_2)\}]^-$, respectively. The positively charged polynuclear complexes were analysed by using the positive-ion mode. The simplest spectra were obtained for the monocationic species $[CoNi_2(tetren)]^+$ and $[CoNi_2(dienpy_2)]^+$ with a single peak at *m*/*z* 709 and 904, respectively. For $[CoNi_3]^{3+}$, the mass spectrum indicates undoubtedly the presence of the molecular peaks at *m*/*z* 1505.9 and 707.5 ascribed to $[Co(CN)_3\{CN{-}Ni(dipropy_2)\}_3]^{2+}$ and $\{[Co(CN)_3\{CN{-}Ni(dipropy_2)\}_3](ClO_4)\}^+$. An additional peak at *m*/*z* 959.0, which was consistent with $[Co(CN)_4\{CN{-}Ni(dipropy_2)\}_2]^+$, is also present and can be considered as a residual entity induced by the technique. The results obtained for $CoNi_5$ are slightly more complex but once again the molecular peaks are visible in the spectrum at *m*/*z* 618 and 439 for $\{[Co(CN)\{CN{-}Ni(tetren)\}_5](ClO_4)_4\}^{3+}$ and $\{[Co(CN)\{CN{-}Ni(tetren)\}_5](ClO_4)_3\}^{4+}$, respectively. Other peaks are also present in the spectrum, which are attributed to $[CoNi_4]^{2+}$ ($\{[Co(CN)\{CN{-}Ni(tetren)\}_4](ClO_4)_3\}^{2+}$; *m*/*z* 726), $[CoNi_4]^+$ ($\{[Co(CN)\{CN{-}Ni(tetren)\}_4](ClO_4)_4\}^+$; *m*/*z* 1607), $[CoNi_3]^{2+}$ ($\{[Co(CN)\{CN{-}Ni(tetren)\}_3](ClO_4)\}^{2+}$; *m*/*z* 528), $[CoNi_3]^+$ ($\{[Co(CN)\{CN{-}Ni(tetren)\}_3](ClO_4)_2\}^+$; *m*/*z* 1158) and $[CoNi_2]^+$ ($[Co(CN)\{CN{-}Ni(tetren)\}_2]^+$; *m*/*z* 709). Finally, the mass spectrum of $[CoNi_6]^{9+}$ displays the molecular peak at *m*/*z* 1199 attributed to the dication $\{[Co\{CN{-}Ni(tetren)\}_6](ClO_4)_7\}^{2+}$.

All these data provide additional evidence of the nature of the polynuclear species and demonstrate their thermodynamic stability in solution.

Magnetic studies: Magnetic studies were performed for all the mononuclear and polynuclear complexes described above and most of them are discussed below.

After the description of the magnetic properties of the CrNi complex ($S = 5/2$), the only one obtained here with the paramagnetic hexacyanochromate(III), $[Cr^{III}(CN)_6]^{3-}$, specific attention will be paid to the mononuclear nickel complexes and to the $CoNi_x$ species ($x = 1$, 2, 3, 5) prepared from a diamagnetic $[Co^{III}(CN)_6]^{3-}$ core. The other Cr^{III} derivatives were (Part 1[7]) or will be (Part 3[9]) discussed elsewhere. With respect to the CrNi compound, the $\chi_M T$ product (χ_M is the molar magnetic susceptibility) increases continuously when cooling down from room temperature to 10 K (Figure 10).

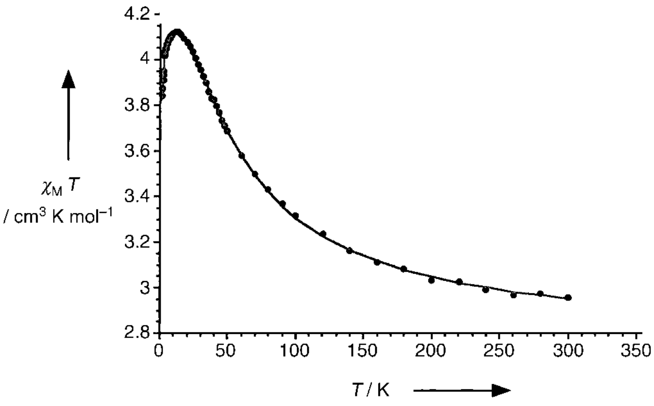


Figure 10. Thermal dependence of the $\chi_M T$ for CrNi.

The $\chi_M T$ value at 300 K is 2.9 $cm^3 mol^{-1} K$ (a little larger than the one expected for two magnetically isolated spins 3/2 [Cr^{III}] and 1 [Ni^{II}]: 2.875 $cm^3 mol^{-1} K$ with $g = 2$). It becomes 4.12 $cm^3 mol^{-1} K$ at 12 K (a little less than 4.375, the value calculated for ferromagnetically coupled spins and $g = 2$) before decreasing at temperatures below 10 K. All these features are consistent with the occurrence of a ferromagnetic exchange coupling between the chromium(III) and the nickel(II) ions (as expected from the orthogonality of their magnetic orbitals); the ground spin state is 5/2. A least-squares fit of the susceptibility data to an analytical expression derived from the spin Hamiltonian $\mathcal{H} = -J S_{Cr} S_{Ni}$ ($S_{Cr} = 3/2$, $S_{Ni} = 1$) leads to $J = +18.5\ cm^{-1}$, $g = 1.97$ and $R = 4 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_i[(\chi_M)_{obs}(i) - (\chi_M)_{calcd}(i)]^2 / \Sigma_i[(\chi_M)_{obs}(i)]^2$). The computed curve matches very well with the data in the temperature range 10–300 K as indicated by the low value of R. It is also possible to reproduce the decrease below 10 K, to include in the analytical expression the zero-field splitting D of the ground state and some intermolecular interaction (zJ'), using a mean field term ($T - zJ'$). The best fit values are then $J = +18.5\ cm^{-1}$, $g = 1.97$, $D = -0.16\ cm^{-1}$ (negative) and $zJ' = -0.15\ cm^{-1}$, indicating significantly weak anisotropy and an antiferromagnetic interaction between nearest neighbours. On the other hand, the molar magnetisation as a function of the applied field at $T = 2$ K gives the saturation value corresponding to the spin ground state, S_G. We find (Figure 11) 5 μ_B corresponds to the expected ground state spin, $S_G = 5/2$. The first magnetisation curve is successfully compared to the corresponding Brillouin function for a spin 5/2. The exchange coupling J is quite strong for two spins 3/2 and 1, far more than 5 Å. It will be compared to those obtained in other hexacyanochromate $CrNi_x$ ($x = 2$, 6) complexes and used to establish magneto-structural correlation in Part 3 of the series.[9]

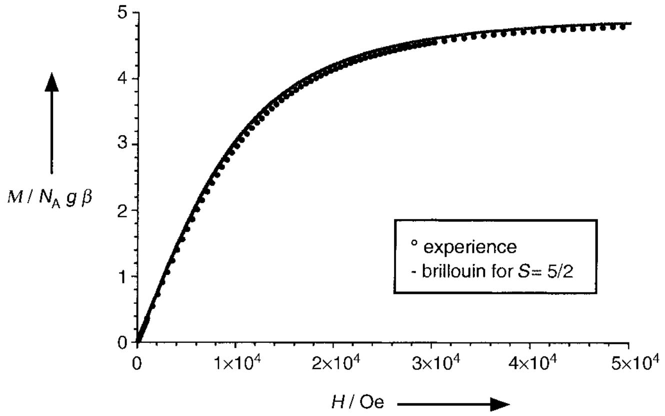


Figure 11. Field dependence of the magnetisation at 2 K for CrNi; the solid lines correspond to the Brillouin functions for $S = 5/2$.

The mononuclear Ni^{II} compounds were studied as reference species to evaluate the magnetic parameters of a single complex. Indeed, the ground state anisotropy of a polynuclear cluster (uniaxial D, rhombic E and higher terms in the Hamiltonian) is a function of several parameters such as 1) the local anisotropy of each of the metallic ions, 2) the exchange anisotropy, and 3) the overall structural anisotropy. Only preliminary results concerning the mononuclear Ni^{II} complexes **1, 2** and **3** are given here.

The magnetic properties of the three mononuclear compounds **1**–**3** are in agreement with paramagnetic species ($S = 1$) of high anisotropy. The $\chi_M T$ product is constant from high temperature to 15 K and then decreases continuously. The values of $\chi_M T$ (1.22, 1.08 and 1.11 $cm^3 mol^{-1} K$, for **1**–**3**, respectively) are higher than the calculated value for an isolated $S = 1$ and $g = 2$ ($\chi_M T = 1\ cm^3 mol^{-1} K$) system, which leads to mean g values of 2.20, 2.07 and 2.10 for **1**, **2** and **3**, respectively. The complete study of electronic aspects of the anisotropy of the mononuclear complexes, data for which was extracted from the magnetisation measurements and compared to high-frequency EPR results, is in progress and will be reported elsewhere. With regard to the hexacyanocobaltate(III) derivatives, which have a diamagnetic core, the magnetic studies allow the evaluation of the Ni–Ni interaction, through the long diamagnetic NC-Co-CN bridge (more than 10 Å), with the next-nearest neighbours, and the determination of individual anisotropic factors of the Ni^{II} or Cu^{II} in a cluster. In all the cases, CoNi, $CoNi_2$(tetren), $CoNi_2(dienpy_2)$, $CoNi_3$, $CoNi_5$, $CoNi_6$, as well as $CoCu_2$ and $CoCu_3$ behave as paramagnetic isolated Ni^{II} or Cu^{II} species with weak intramolecular interactions. The $\chi_M T$ product of the nickel(II) species are reported in Figure 12. The values are constant from room temperature to 15 K and then decrease at low temperature. The $\chi_M T$ values at 300 K for CoNi (1.10), $CoNi_2$ (2.11), $CoNi_3$ (2.75), $CoNi_5$ (5.13) and $CoNi_6$ (5.83 $cm^3 mol^{-1} K$) are in agreement with one, two, three, five and six isolated nickel ions, respectively, and $g \approx 2$. Similar results were noted in the first magnetisation curve at 2 K with five series of data corresponding to compounds containing between one and six isolated nickel ions (Figure 13); the pentanuclear species, $CoNi_4$, is the only missing complex of the complete family.

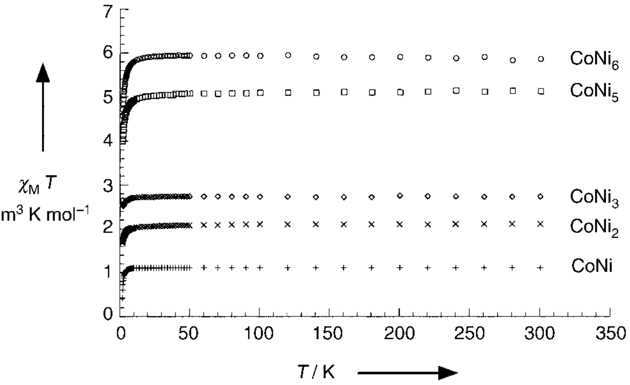


Figure 12. Thermal dependence of the $\chi_M T$ product for CoNi, $CoNi_2$, $CoNi_3$, $CoNi_5$ and $CoNi_6$.

The values of the computed exchange coupling were determined for all the "$CoNi_x$" species ($x = 2$) and the results are as follows: -0.13 ($g = 2.02$), -0.10 ($g = 2.04$), -0.43 ($g = 1.95$), -0.15 ($g = 2.02$) and $-0.45\ cm^{-1}$ ($g = 2.0$), for $CoNi_2$(tetren), $CoNi_2(dienpy_2)$, $CoNi_3$, $CoNi_5$ and $CoNi_6$, respectively. This indicates that the exchange interaction to the second neighbours (through the NC-Co^{III}-CN bridge) is weak

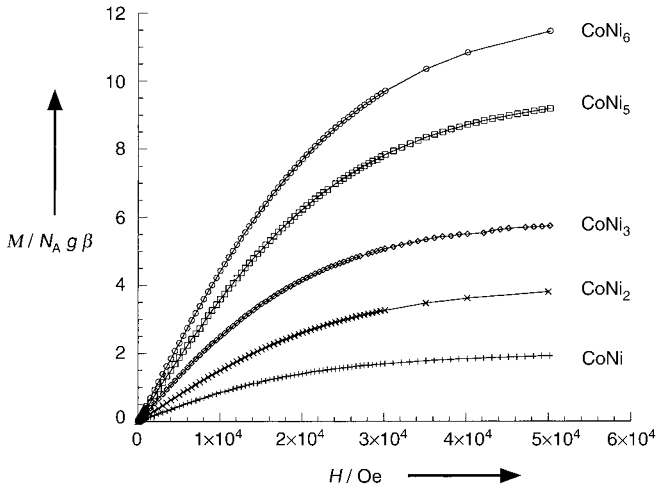


Figure 13. Field dependence of the magnetisation at 2 K for CoNi, $CoNi_2$, $CoNi_3$, $CoNi_5$ and $CoNi_6$; the solid lines correspond to the Brillouin functions for 1, 2, 3, 5 and 6 isolated nickel ions.

(compared to that to the first neighbours) and is directly correlated to the N-C-Ni angle, and that this parameter might be omitted in the magnetic studies of high-spin chromium-centred complexes.

The $CoNi_3$ complex presents an interesting geometry with three metallic ions in a triangle that are weakly antiferromagnetically coupled. This would have been viewed as an example of spin frustration if the exchange coupling constant had been more significant. Very low-temperature studies are in progress to analyse more deeply the frustration effect.

With regard to the $CoCu_2$–$CoCu_3$ complexes, similar experiments were performed that showed that the thermal dependence of $\chi_M T$ is characteristic of a paramagnetic species. $\chi_M T$ is constant with an experimental value of 2.15 $cm^3 mol^{-1} K$ in agreement with five isolated copper(II) metallic ions (the expected value is 2.14 $cm^3 mol^{-1} K$ for five separated spin = 1/2 and $g = 2.14$). At low temperature, below 30 K, the $\chi_M T$ curve decreases continuously indicating the occurrence of either intra- and/or intermolecular antiferromagnetic interactions between the spin carriers. The best fit was obtained with $J = -0.48$ cm^{-1} and $g = 2.15$ and displayed an agreement factor $R = 9.6 \times 10^{-6}$ (the distinction between *cis* and *trans* CN-Co-CN bridges was not taken into consideration). The antiferromagnetic intramolecular interaction is smaller than the one obtained for the $CoCu_6$ complex ($J = -0.85$ cm^{-1}); the difference between the two coupling constants is due to the different values of the C-N-Cu angle (see Part 3 of this series).[9]

Conclusion

A rational strategy for the synthesis of polynuclear species based on hexacyanocobaltate(III) center surrounded by Cu^{II} and Ni^{II} ions is described herein. Among the nine possible geometries for an hexacyanometalate core, seven were obtained. Thus, molecules such as CrNi, $CoCu_2$ and $CoCu_3$, in addition to the series of $CoNi_x$ complexes ($x = 1, 2, 3, 5, 6$): CoNi, $CoNi_2$, $CoNi_3$, $CoNi_5$ and $CoNi_6$ were synthesised and fully characterised. This family of compounds is the main focus of the present paper, and demonstrates the possibility to obtain selectively, bi-, tri-, tetra-, hexa- or heptanuclear complexes by tuning the synthetic parameters (ligand, counter anion, stoichiometry). It should be possible to extend the synthetic strategy to other metallic polycyanometalate precursors and especially to hexacyanochromate(III), which should in turn allow the preparation of anisotropic high-spin molecules such as CrNi, $CrNi_2$, $CrNi_3$ and $CrNi_5$ that might behave as single-molecule magnets. We have already demonstrated the feasibility of this approach and the analogy of hexacyanochromate(III) and hexacyanocobaltate(III) through the description of the CrNi complex. The trinuclear $CrNi_2$ compounds are fully described in Part 3[9] of this series together with the study of the intramolecular exchange coupling. The other species, especially $CrNi_3$, will be described elsewhere.

Experimental Section

Warning! Although we have experienced no difficulties with the perchlorate salts and complexes described, these are potentially explosive and should be handled in small amounts and with caution. $K_3[Cr(CN)_6]$ was synthesised by using literature methods.[35, 36] The ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane ($dienpy_2$) and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane ($dipropy_2$) were obtained following experimental methods already described.[25,26] All other reagents were purchased as reagent-grade chemicals and used without further purification. All solvents were analytical-grade quality.

$[Ni(tetren)(ClO_4)](ClO_4)$ (1): Potassium hydroxide (2.26 g, 40.5 mmol; 5 equiv) dissolved in a minimum of water was added to a solution of tetraethylenepentamine hydrochloride salt (tetren · 5 HCl) (3 g, 8.1 mmol) in water (10 mL). After the mixture had been stirred for 10 min, the product was extracted with dichloromethane. The organic phase was dried on potassium sulfate, and the filtrate and the solvent were evaporated under reduced pressure. Nickel perchlorate salt (1.5 g, 4.1 mmol) dissolved in water was added to the tetren (1.2 g, 6.3 mmol) in H_2O/CH_3CN (1:1; 10 mL) mixture. The blue solution was left standing for a few days. Recrystallisation in the presence of sodium perchlorate salt allowed the formation of purple crystals of the mononuclear nickel complex, which were washed with ethanol. $M_r = 446.91$, 23% yield; IR (KBr): $\tilde{\nu} = 965, 1035, 1456$ and 1593, (ligand), 522 and 1080 cm^{-1} (ClO_4); elemental analysis calcd (%) for $C_8H_{23}NiN_5Cl_2O_8$: C 21.50, H 5.19, N 15.67, Ni 13.13, Cl 15.87; found: C 21.16, H 5.29, N 15.40, Ni 12.90, Cl 15.55.

$[Ni(dienpy_2)(H_2O)](ClO_4)_2$ (2): Nickel perchlorate salt (3.2 g, 9.4 mmol; 1 equiv) dissolved in water was added to a solution of 1,9-bis(2-pyridyl)-2,5,8-triazanonane ($dienpy_2$) (3 g, 9.6 mmol) in water (10 mL). After the mixture had been stirred for 10 min, the solution was left standing for a few days. Blue crystals appeared which were characteristic of the mononuclear nickel complex. 59% Yield; IR (KBr): $\tilde{\nu} = 1641, 1608, 1492, 1438, 522$ (ligand), 1085 cm^{-1} (ClO4); elemental analysis calcd (%) for $C_{16}H_{25}NiN_5O_9Cl_2 \cdot H_2O$: C 33.19, H 4.70, N 12.10, Ni 10.14, Cl 12.25; found: C 33.10, H 5.47, N 12.14, Ni 9.30, Cl 11.90.

$[Ni(dipropy_2)(H_2O)](BF_4)_2$ (3): Nickel tetrafluoroborate salt (3.2 g, 9.4 mmol; 1 equiv) dissolved in water was added to a solution of 1,11-bis(2-pyridyl)-2,6,10-triazaundecane ($dipropy_2$) (3 g, 9.6 mmol) in water (10 mL). After the mixture had been stirred for 10 min, the solution was left standing for a few days. Dark blue crystals of the mononuclear nickel complex appeared. $M_r = 563.77$, 68% Yield; IR (KBr): $\tilde{\nu} = 1641, 1608, 1492, 1438, 522$ (ligand), 1085 cm^{-1} (BF_4); elemental analysis calcd (%) for $C_{18}H_{29}NiN_5O$: C 38.35, H 5.18, N 12.42, Ni 10.41, B 3.84, F 26.96; found: C 38.20, H 5.21, N 12.43, Ni 10.32, B 3.82, F 26.86.

$[Cr(CN)_5\{CNNi(dienpy_2)\}][AsPh_4]$ (CrNi): A solution of tris(2-amino)-ethylamine (0.95 g, 6.5 mmol) in water—acetonitrile (1:1, 10 mL) was added to a solution of 1,9-bis(2-pyridyl)-2,5,8-triazanonane ($dienpy_2$) (1 g, 3.5 mmol) in water (20 mL). The mixture was stirred for 20 min before hexacyanochromate potassium salt (0.325 g, 1 mmol) dissolved in a minimum amount/volume of water was added. The solution was left standing for a few days in the presence of tetraphenylarsonium, and the resulting light pink fragile plates were collected and washed with ethanol. Yield: 63 %; IR (KBr): $\tilde{\nu} = 2120$, 2129 and 2151 cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{46}H_{43}AsCrNiN_{11}$](H_2O)$_3$: C 55.89, H 4.89, N 15.59, Cr 5.26, Ni 5.94, As 7.58; found: C 55.50, H 4.66, N 15.14, Cr 5.75, Ni 5.76, As 7.52.

[Co(CN)$_5${CNNi(dienpy$_2$)}][AsPh$_4$] (CoNi): This complex was prepared following the procedure described for [Co(CN)$_5${CNNi(dienpy$_2$)}][AsPhi$_4$], using hexacyanocobaltate as the starting precursor. The solution was left standing for a few days in the presence of tetraphenylarsonium, and the resulting pink-purple product was collected and washed with ethanol. Yield: 68 %; IR (KBr): $\tilde{\nu} = 2119$, 2128 and 2157 cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{46}H_{43}AsCoNiN_{11}$](H_2O)$_3$: C 55.44, H 4.96, N 15.46, Co 5.91, Ni 5.89, As 7.52; found: C 55.95, H 4.95, N 14.12, Co 5.38, Ni 5.35, As 8.24.

[Co(CN)$_4${(CNNi(tetren)$_2$}]Cl (CoNi$_2$-tetren): Nickel chloride (755 mg, 3.17×10^{-3} mol) was added to a solution of tetren · 5 HCl (tetraethylenepentamine pentahydrochloride) (1.12 g, 3.01×10^{-3} mol) in water (20 mL). The mixture was stirred for 10 min before potassium hexacyanocobaltatate (0.150 g, 4.6×10^{-4} mol) dissolved in a minimum amount of water was added. The purple hexagonal crystals were collected and washed with water. Yield: 54 %; IR (KBr): $\tilde{\nu} = 2117$, 2131 and 2142 cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{22}H_{46}CoNi_2N_{16}Cl$]($H_2O$)$_7$: C 30.28, H 6.88, N 25.69, Co 6.75, Ni 13.45, Cl 4.06; found: C 30.41, H 6.79, N 25.52, Co 6.61, Ni 13.24, Cl 3.99.

[Co(CN)$_4${(CNNi(dienpy$_2$)$_2$}](BF$_4$)(H$_2$O)$_9$ (CoNi$_2$(dienpy$_2$)): Nickel tetrafluoroborate (0.55 g, 1.6 mmol, 0.9 equiv) was added to a solution of dienpy$_2$ (0.514 g 1.8 mmol) in water – acetonitrile (1:1; 10 mL). The mixture was stirred for 10 min before potassium hexacyanocobaltate(III) (0.22 g, 0.66 mmol, 0.4 equiv) dissolved in a minimum of water was added. The solution was left standing for a few days to give pink-purple crystals. Yield: 78 %; IR (KBr): $\tilde{\nu} = 2136$ and 2138 cm^{-1} (sh) (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{38}H_{46}CoNi_2N_{16}BF_4$]($H_2O$)$_8$: C 40.24, H 5.51, N 19.76, Co 5.20, Ni 10.35, B 0.95, F 6.70; found: C 40.11, H 4.91, N 19.79, Co 3.67, Ni 8.92, B 1.48, F 5.02.

[Co(CN)$_3${(CN)Ni(dipropy$_2$)}$_3$](BF$_4$)$_3$ (CoNi$_3$): Potassium hexacyanocobaltate(III) (56 mg, 0.17 mmol) dissolved in a minimum amount of water was carefully added to a solution of [Ni(dipropy$_2$)(BF$_4$)$_2$] (0.5 g, 0.88 mmol) in water – acetonitrile (1:1; 10 mL). After slow evaporation of the solvent, purple cubic crystals appeared. $M_r = 1699.99$; yield 75 %; IR (KBr): $\tilde{\nu} = 2141$ and 2172 cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{60}H_{81}CoNi_3N_{21}B_3F_{12}$]($H_2O$)$_6$: C 42.39, H 5.51, N 17.30, Co 3.47, Ni 10.36, B 1.91, F 13.41; with (KBF$_4$)$_{0.65}$, C 40.45, H 5.26, N 16.51, Co 3.31, Ni 9.88, B 2.21, F 15.57; found: C 40.48, H 5.13, N 16.55, Co 3.28, Ni 9.56, B 2.18, F 13.56.

[Co(CN){(CN)Ni(tetren)}$_5$](ClO$_4$)$_7$ (CoNi$_5$): NaOH (404 mg, 1×10^{-2} mol) followed by nickel perchlorate (502 mg, 1.4×10^{-3} mol) was added to a solution of tetren · 5 HCl (tetraethylene pentamine pentahydrochloride) (0.747 g, 2×10^{-3} mol) in water (20 mL). The mixture was stirred for 10 min before silver perchlorate (2.08 g, 1×10^{-2} mol) was added to eliminate the chloride ions. The solution was stirred for 1 h in the dark, then the precipitate was filtered off and acetonitrile (5 mL) was added. Potassium hexacyanocobaltate(III) (0.111 g, 3.34×10^{-4} mol) dissolved in a minimum of water was added and the solution was left standing for a few days and filtered from time to time. The resulting pink-purple crystals were collected. Yield: 69 %; IR (KBr): $\tilde{\nu} = 2149$ cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for [$C_{46}H_{116}CoNi_5N_{31}Cl_7O_{28}$]($H_2O$): C 25.47, H 5.44, N 20.02, Co 2.72, Ni 13.53, Cl 11.44; found: C 25.46, H 5.49, N 19.89, Co 2.72, Ni 12.78, Cl 11.30; X-ray diffraction: chemical formula: $C_{92}H_{234}N_{62}Co_2Ni_{10}Cl_{14}O_{58}$, Fw = 4338.48, monoclinic, space group = $P2_1$, $a = 17.186$, $b = 23.374$, $c = 22.427$ Å, $\beta = 93.258°$, $V = 9318.4$ Å^3, $Z = 4$.

[Co(CN)$_4${CN–Cu(tren)$_2$}][Co(CN)$_3${CN–Cu(tren)$_3$}](ClO$_4$)$_4$ (CoCu$_2$–CoCu$_3$): A solution of tris(2-amino)ethylamine (0.3 g, 2 mmol) in water – acetonitrile (1:1, 20 mL) to a solution of copper perchlorate (0.75 g, 2 mmol) in water – acetonitrile (1:1, 20 mL). The mixture was stirred for 10 min before potassium hexacyanocobaltate(III) (0.325 g, 1 mmol) dissolved in a minimum of water was added slowly. The solution was left standing for a few days and the resulting blue hexagonal crystals were collected and washed with ethanol. Yield: 37 %; IR (KBr): $\tilde{\nu} = 2126$, 2132 and 2162 cm^{-1} (ν_{as}(CN)); elemental analysis calcd (%) for $C_{42}H_{98}Co_2Cu_5N_{32}Cl_4O_{20}$: C 25.89, H 5.07, N 23.00, Co 6.05, Cu 16.30, Cl 7.28; found: C 22.97, H 4.37, N 21.10, Co 5.48, Cu 14.52, Cl 8.66; X-ray diffraction: chemical formula: $C_{90}H_{252}CrCu_{12}N_{62}Cl_{21}O_{84}$, Fw = 5106.36, crystal system: monoclinic, space group = $P2_1/c$, $a = 8.269(3)$ $b = 45.351(5)$, $c = 12.200(2)$ Å, $V = 4556(2)$ Å^3, $Z = 3$, $R(R\text{w}) = 0.128$ (0.129).

Physical characterisations: Electronic spectra were obtained with a UV 210 PC Shimadzu spectrophotometer. IR spectra were recorded between 4000 and 250 cm^{-1} on a Bio-Rad FTS 165 FT-IR spectrometer in KBr pellets. DC magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer equipped with a 5 T magnet and operating in the temperature range 1.8 – 400 K. The powdered samples (10 – 50 mg) were placed in a diamagnetic sample holder and the measurements realised in a 200 Oe applied field by using the extraction technique. Before analysis, the experimental susceptibility was corrected for diamagnetism using Pascal constants[1] and for the temperature-independent paramagnetism (TIP) of the transition metals. ESI-MS measurements were performed in solution using a modified NERMAG R 10-10 quadrupole mass spectrometer, equipped with an Analytica of Brandford electrospray source. The range of the instrument was m/z 10 – 2000. The spectra were recorded over the range m/z 2000, in steps of m/z 1. The output signal of the electron multiplier was transferred to a PC for treatment of the spectra. The MST mass treatment program was developed in the Laboratoire de Chimie Structurale Organique et Biologique according to the algorithm of Reinhold et al.[37] The complexes were analysed in the positive mode after dilution at approximately 10^{-4} mol L^{-1} in dry acetonitrile. The entry capillary voltage used was − 2700 V. The samples were infused into the source using a Harvard 11 syringe pump at a flow rate of 2 µL min^{-1}. The exit capillary voltage was 60 V and the first skimmer voltage was 50 V. The N_2 drying gas temperature was 75 °C with a pressure of 68.95×10^3 Pa at 5 L min^{-1}.

Crystallographic studies: The CrNi structure was recorded on a CCD diffractometer in Versailles. All other structures were solved on a CAD 4 diffractometer. Suitable crystals for X-ray crystallography were directly obtained from the reaction medium or by recrystallisation from water – acetonitrile solutions. For all the structures described, accurate cell dimensions and orientation matrices were obtained by least-square refinements of 25 accurately centred reflections on a Nonius CAD 4 diffractometer equipped with graphite-monochromated Mo$_{K\alpha}$ radiation. No significant variations were observed in the intensities of two checked reflections during data collection. Absorption corrections were applied by using the ψ scan method. Computation was performed using the PC version of Crystals.[38] Scattering factors and corrections for anomalous dispersion were taken from Cromer.[39] The structures were solved with SHELX 86[40] (Fourier maps technique) and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms, when sufficient data were available. Full crystallographic data and details of the refinements are given in Table 1.

CCDC-187301 (Ni(tetren)), CCDC-187299 (Ni(dienpy$_2$)), CCDC-187300 (Ni(dirpopy$_2$)), CCDC-186515 (CrNi), CCDC-187296 (CoNi$_2$(tetren)), CCDC-187298 (CoNi$_2$(dienpy$_2$)) and CCDC-187297 (CoNi$_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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