

Use of the Di-2-pyridyl Ketone/Acetate/Dicyanamide “Blend” in Manganese(II), Cobalt(II) and Nickel(II) Chemistry: Neutral Cubane Complexes

Giannis S. Papaefstathiou,^[a] Albert Escuer,^[b] Franz A. Mautner,^[c] Catherine Raptopoulou,^[d] Aris Terzis,^[d] Spyros P. Perlepes,^{*[a]} and Ramon Vicente^{*[b]}

Keywords: Cobalt(II) cubanes / Dicyanamide complexes / Di-2-pyridyl ketone / Magnetic properties / Manganese(II) cubanes / Nickel(II) cubanes

The use of di-2-pyridyl ketone [(2-py)₂CO]/dicyanamide “blend” in cobalt(II), manganese(II) and nickel acetate chemistry has yielded neutral cubane clusters. The preparation of [Mn₄(O₂CMe)₂{N(CN)₂[(2-py)₂C(OH)O]₄·2(2-py)₂CO·4H₂O (**1**) and [M₄(O₂CMe)₂{N(CN)₂[(2-py)₂C(OH)O]₄·10H₂O [M = Ni (**2**), Co (**3**)] was achieved by the reaction of [M(O₂CMe)₂·4H₂O with (2-py)₂CO and Na[N(CN)₂] in MeOH/H₂O (1:5, v/v) at room temperature. The metal(II)-mediated hydrolysis of (2-py)₂CO to give the coordinated monoanion of the hydrate *gem*-diol form involves a nucleophilic attack of H₂O on the carbonyl group. In the case of the cobalt reaction system, there is a second product. Upon employing an excess of (2-py)₂CO, long reaction times, reflux conditions and high dilution, slow oxidation of Co^{II} takes place leading to the isolation of the mononuclear cobalt(III) complex [Co{(2-py)₂C(OH)O]₂][N(CN)₂·4H₂O (**4**) in yields higher than 70 %. The structures of **1**, **2** and **4** have been solved by single-crystal X-ray diffraction studies, while a

unit-cell determination indicated that complex **3** is isostructural with **2**. The tetranuclear cluster molecules of **1** and **2** have cubane [M₄(μ₃-OR)₄]⁴⁺ cores with divalent metal atoms and deprotonated oxygen atoms [originating from the (2-py)₂C(OH)O[−] ligands] occupying alternate vertices. The centrosymmetric [Co{(2-py)₂C(OH)O]₂]⁺ cation of complex **4** has an octahedral structure with the (2-py)₂C(OH)O[−] ligands adopting the tridentate *N,O,N'*-chelating coordination mode. The magnetic properties of **1–3** have been studied by variable-temperature dc magnetic susceptibility techniques. The studies indicate weak antiferromagnetic coupling for **1** and ferromagnetic behaviour for **2** and **3**. A three-*J* model was found to be adequate for describing the thermal variation of the molar magnetic susceptibilities of **1** and **2**. The magnetochemical results have been compared with literature data.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

There continues to be great interest in the synthesis and study of polynuclear metal complexes (clusters) containing paramagnetic 3d-metals in intermediate oxidation states.^[1] There are various reasons for this, not least of which is the aesthetically pleasing nature of some of these species.^[2] From an applications point of view, however, efforts in this area are part of the continuing search for new examples of molecular species which can function as nanoscale magnetic particles or so-called single-molecule magnets (SMMs).^[3] These zero-dimensional (0D) systems display slow relax-

ation of their magnetisation vectors as a result of the combination of a large ground state (*S*) and an Ising (or easy-axis) type of magnetoanisotropy.^[3] Thus, such molecules exhibit magnetisation hysteresis loops, i.e. the classical behaviour of a magnet. The unusual quantum phenomena^[4] such molecules display have also led researchers to propose that the molecules could be used as Qbits in quantum computers.^[5] The most studied examples of SMMs are the [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] compounds with *S* = 10.^[3] Another compound which has been intensely investigated for its SMM behaviour is [{Fe₈O₂(OH)₁₂(tacn)₆]Br₇(H₂O)]·Br·8H₂O (tacn = 1,4,7-triazacyclononane),^[3] characterised by an *S* = 10 ground state. Since these first discoveries, other oxidation levels^[6] in the Mn₁₂ family and other Mn_x^[2a,2d,3,7] and M_x (M = V^{III},^[8] Fe^{II},^[9] Fe^{III},^[10] Co^{II},^[11] Ni^{II}^[12]) SMMs, including mixed-metal systems,^[13] have been prepared with *S* values ranging from 3 to 5^{1/2}.

The future health of the field of high-spin molecules and the chances of identifying new SMMs will both benefit from the development of new synthetic methodologies for 3d-metal clusters. With this in mind, our group^[9b,14,15] and

[a] Department of Chemistry, University of Patras, 265 04 Patras, Greece
E-mail: perlepes@patreas.upatras.gr

[b] Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
E-mail: ramon.vicente@qi.ub.es

[c] Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, 8010 Graz, Austria

[d] Institute of Materials Science, NCSR “Demokritos”, 153 10 Aghia Paraskevi Attikis, Greece

others^[16] have been exploring “binary ligand blend” reactions involving (i) the monoanion $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ or the dianion $(2\text{-py})_2\text{CO}_2^{2-}$ of the *gem*-diol form of di-2-pyridyl ketone $(2\text{-py})_2\text{CO}$ (the formulae of these ligands are shown in Figure 1) and carboxylates, and (ii) the monoanion $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-$ of the hemiacetal form of $(2\text{-py})_2\text{CO}$ (Figure 1) and carboxylates, with the belief that they might foster formation of discrete polynuclear metal systems. The reactions of $(2\text{-py})_2\text{CO}$ with metal ions have been well studied over the years.^[15–17] Water and alcohols (ROH) have been shown to add to the carbonyl group upon coordination of the 2-pyridyl ring to the ligands forming the ligands $(2\text{-py})_2\text{C}(\text{OH})_2$ [the *gem*-diol form of $(2\text{-py})_2\text{CO}$] and $(2\text{-py})_2\text{C}(\text{O}-\text{R})(\text{OH})$ [the hemiacetal form of $(2\text{-py})_2\text{CO}$], respectively. The neutral ligands $(2\text{-py})_2\text{C}(\text{OH})_2$ and $(2\text{-py})_2\text{C}(\text{OR})(\text{OH})$ coordinate to the metal centres as tridentate N,N',O chelates, with the M–O bond often being weak. Therefore, both neutral ligands do not hold much interest from the cluster formation point of view.^[14] Completely different and much more interesting (for cluster chemistry) coordination modes are seen when the ligands $(2\text{-py})_2\text{C}(\text{OH})_2$ and $(2\text{-py})_2\text{C}(\text{O}-\text{R})(\text{OH})$ are deprotonated. Upon deprotonation the latter becomes monoanionic, while the former can exist either as monoanionic or dianionic. The presence of deprotonated hydroxyl group(s) leads to a great coordinative flexibility due to the well known ability of the negatively charged oxygen atom to bridge two or three metal ions. The immense structural diversity displayed by the complexes reported stems in part from the ability of $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, $(2\text{-py})_2\text{CO}_2^{2-}$ and $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-$ to exhibit no less than nine distinct bridging coordination modes ranging from μ_2 to μ_5 .^[14] Carboxylates are employed for two reasons in the above mentioned “ligand blends”. Firstly, they are able to deprotonate the hydroxyl group(s) of $(2\text{-py})_2\text{C}(\text{OH})_2$ and $(2\text{-py})_2\text{C}(\text{OR})(\text{OH})$ under mild conditions (the use of hydroxides often complicates the reactions). Secondly, they are flexible ligands, a consequence of their ability to adopt a number of different ligation modes, both terminal and bridging as well as both monodentate and bidentate. Thus, the $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-/\text{R}'\text{CO}_2^-$, $(2\text{-py})_2\text{CO}_2^{2-}/\text{R}'\text{CO}_2^-$ and $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-/\text{R}'\text{CO}_2^-$ “blends” (R = Me, Et; R' = Me, CF₃, Ph) have led to a variety of Mn, Fe, Co, Ni and Cu clusters with nuclearities ranging from three to fourteen and with interesting magnetic properties.^[14–16]

Three years ago we decided to incorporate azido ligands, N_3^- , into the 3d-metal carboxylate chemistry of $(2\text{-py})\text{CO}_2^{2-}$, $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ and $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-$, i.e. to study the “ternary ligand blend” reaction systems $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, $(2\text{-py})_2\text{CO}_2^{2-}$ or $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-/\text{R}'\text{CO}_2^-/\text{N}_3^-$, as a means of introducing specifically ferromagnetic components into the superexchange schemes, thus increasing the ground state *S* values of the clusters.^[9b,18] For example, we reported^[9b,18b,18c] that the reactions of $\text{M}(\text{O}_2\text{CMe})_2 \cdot x\text{H}_2\text{O}$ (M = Co, Ni, *x* = 4; M = Fe, *x* = 0) with $(2\text{-py})\text{CO}$ and N_3^- in DMF or MeCN with heating led to the nonanuclear cages $[\text{M}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8\{(2\text{-py})_2\text{CO}_2\}]$ in which the nine M^{II} ions adopt a topology of two square pyramids sharing a common apex. Salient features of the similar structures are

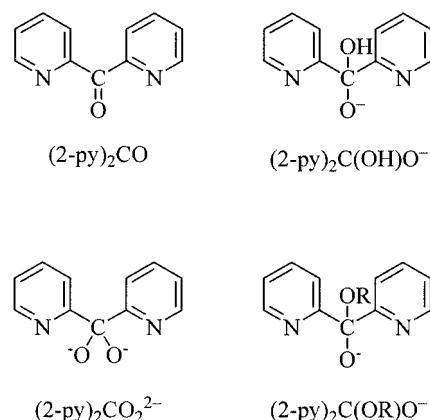


Figure 1. Some of the ligands discussed in the text. Note that the anionic ligands do not exist as free species, they exist only in metal complexes.

the unique $\eta^1:\mu_4$ coordination mode of the azido ligands, the μ_5 coordination mode of $(2\text{-py})_2\text{CO}_2^{2-}$ and the extremely rare coordination number 8 for the central M^{II} ion lying at the common apex of the pyramids. Magnetic studies revealed ferromagnetic coupling mediated by the azido bridges, giving a ground state total *S* value of seven times the local spin in the case of cobalt(II),^[18e] 9 in the case of nickel(II)^[18b] and 14 for the iron(II) cluster.^[9b] It should be mentioned at this point that Mn^{II} , Co^{II} and Ni^{II} clusters containing *only* various anionic forms of $(2\text{-py})_2\text{CO}$ and N_3^- ligands, i.e. non-carboxylate species, are also known.^[19]

Very recently we began a program which can be considered as a modification of the above “ternary ligand blend” approach. We have been exploring the use of the dicyan-amido ligands, $\text{N}(\text{CN})_2^-$ (Figure 2) instead of the azido ligands. The great coordinative flexibility and versatility of the $(2\text{-py})_2\text{CO}$ -based anionic ligands and carboxylates, as well as the μ_2 , μ_3 , μ_4 or μ_5 potential of $\text{N}(\text{CN})_2^-$,^[20] prompted us to combine the three ligands to aim for new types of clusters and/or supramolecular architectures involving repeating cluster units. Our belief was that the simultaneous employment of the three classes of ligands in high-nuclearity 3d-metal chemistry would give extraordinary structural flexibility in the mixed $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, $(2\text{-py})_2\text{CO}_2^{2-}$ or $(2\text{-py})_2\text{C}(\text{OR})\text{O}^-/\text{R}'\text{CO}_2^-/\text{N}(\text{CN})_2^-$ ligand systems (“blends”). The loss of some degree of synthetic control^[1b] may be more than compensated for by the vast diversity of structures expected using the combination of the three ligands. The advantages of using $\text{N}(\text{CN})_2^-$ in place of N_3^- include (i) the possibility of triggering aggregation of preformed species into new, higher-nuclearity products and (ii) the possible diversion of known reaction systems developed using azides to new species as a result of the different flexibility of dicyanamides.

Dicyanamide is currently a ligand of great interest,^[20,21] mainly due to the observation of long-range magnetic ordering in the binary $\alpha\text{-}[\{\text{M}[\text{N}(\text{CN})_2]_2\}_n]$ (M = Cr, Mn, Fe, Co, Ni) compounds.^[20] Also of particular interest is the generation of new $\text{M}^{\text{II}}\text{-N}(\text{CN})_2^-$ architectures through the introduction of coligands into the structures. These ternary

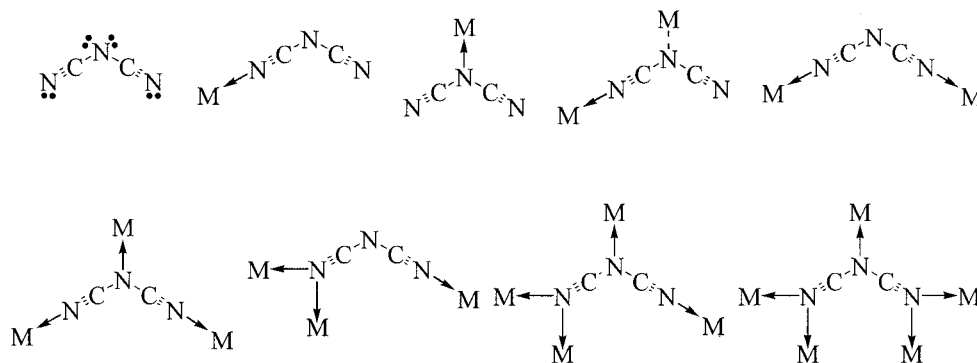


Figure 2. The dicyanamide ion and its crystallographically established coordination modes.

systems exhibit a wide variety of topologies and in a few cases long-range magnetic ordering has been observed at low temperatures.^[20] This anion is a versatile ligand^[20,22] which has been shown, by crystallography, to coordinate to metal ions in various modes (Figure 2), namely monodentate bonding through a nitrile nitrogen, end-to-end bridging through the two nitrile nitrogen atoms, bidentate bridging through one nitrile and the amide nitrogens or by strong coordination of one nitrile nitrogen and semicoordination of the amide nitrogen, tris(monodentate) bridging (μ_3), end-to-end μ_3 bridging with one nitrile nitrogen atom forming a monoatomic bridge as well as an unusual μ_4 mode where one nitrile nitrogen binds to two metal ions and an extremely rare μ_5 mode where each nitrile nitrogen binds to two metal ions. More generally, however, $N(CN)_2^-$ is also a very interesting ligand in the wider context of coordination chemistry due to its ability to undergo metal ion-assisted nucleophilic addition reactions with alcohols and pyrazole generating interesting polydentate ligands.^[23]

The $N(CN)_2^-$ ligand has been used extensively in the synthesis of coordination polymers^[20–22] but has been infrequently used for the synthesis of discrete 3d-metal clusters. We herein report the first use of $N(CN)_2^-$ in 3d-metal carboxylate/(2-py)₂CO chemistry which leads to neutral cubane manganese(II), cobalt(II) and nickel(II) clusters. The syntheses, structures, spectroscopic and magnetic properties of these species are described. A synthetically relevant cobalt(III) complex is also reported.

Results and Discussion

Synthesis

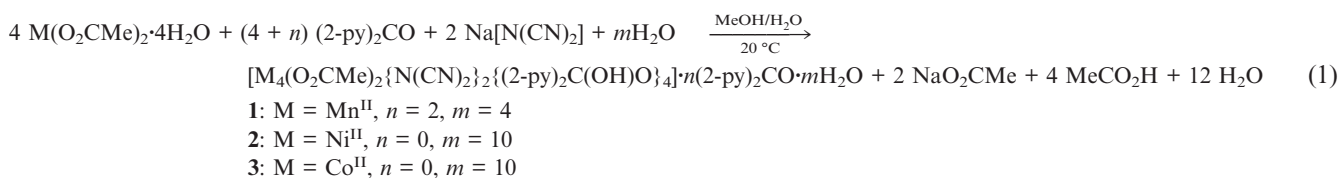
Our general synthetic approach for the isolation of heteroleptic (2-py)₂CO₂²⁻ or (2-py)₂C(OH)O⁻ or (2-py)₂C(OR)O⁻/MeCO₂⁻/ $N(CN)_2^-$ 3d-metal clusters was to treat an excess of the metal acetate with (2-py)₂CO and

$N(CN)_2^-$ in various solvents. Obviously “(2-py)₂C(OH)₂” and “(2-py)₂C(OR)(OH)” can be fully/partially deprotonated by the basic acetate groups and polynuclear M^{II}/(2-py)₂CO₂²⁻, (2-py)₂C(OH)O⁻ or (2-py)₂C(OR)O⁻/MeCO₂⁻/ $N(CN)_2^-$ complexes may result from the reactions as long as the MeCO₂⁻ to (2-py)₂CO ratio is high enough to leave an amount of MeCO₂⁻ in the reaction mixture, given the fact that the anionic forms of (2-py)₂CO, acetate and dicyanamide ligands can adopt a variety of terminal and bridging modes.

The preparation of compounds **1**, **2** and **3** can be achieved by the reaction of $M(O_2CMe)_2 \cdot 4H_2O$ with (2-py)₂CO and Na $[N(CN)_2]$ in MeOH/H₂O ($\approx$ 1:5, v/v) at room temperature. The preparation of these complexes can be summarised by the general balanced Equation (1).

The metal(II)-mediated hydrolysis of (2-py)₂CO to give the monoanion of the hydrate *gem*-diol form involves a nucleophilic attack of H₂O on the carbonyl group. In such reactions it might not be necessary for the carbonyl atom to be coordinated to the metal centre. The induced polarisation from the pyridyl nitrogen atoms might be sufficient.^[14]

A few features of the general chemical Equation (1) deserve comments. First, the incorporation of uncoordinated (2-py)₂CO molecules in **1** is not common and could not be predicted. Presumably, the presence of these molecules satisfies the requirements of the crystal lattice. However, the existence of ligand molecules in their ketone forms can be explained by the fact that the (2-py)₂C(OH)₂ molecules do not exist as free species but exist only within the coordination sphere of metal ions.^[14] The presence of lattice (2-py)₂CO has been established crystallographically^[24] only in complexes $[Cu_2\{(2-py)_2C(OMe)O\}_2(phen)_2]X_2 \cdot 2(2-py)_2CO$, where phen = 1,10-phenanthroline and X = PF₆⁻ or ClO₄⁻. Secondly, the presence of MeOH in the solvent mixture might imply the presence of the monoanion of the hemiacetal form of di-2-pyridyl ketone, i.e. (2-py)₂C(OMe)-



O[−] in the complexes. This is a common synthetic feature in (2-py)₂CO-based coordination chemistry.^[14,17j–17l,19a,19c,19d] However, only (2-py)₂C(OH)O[−] ligands are present in complexes **1–3**. This can be rationalised on the basis of the crystallisation method used. The complexes were crystallised by slow evaporation at room temperature of a solvent mixture consisting of MeOH and H₂O in a 1:5 volume ratio. This means that precipitation/crystallisation of the clusters was effected from *essentially aqueous media* (i.e., MeOH-free) and, thus, the coordination of *only* (2-py)₂C(OH)O[−] might be expected. Thirdly, the “wrong” stoichiometry, i.e. $M(O_2CMe)_2 \cdot 4H_2O / (2-py)_2CO / Na[N(CN)_2] = 2:1:1$, employed for the preparation of **1**, **2** and **3** (see Exp. Sect.) compared with that required by Equation (1) was due to our desire to doubly deprotonate the *gem*-diol form of (2-py)₂CO and to prepare complexes of (2-py)₂CO₂^{2−}. However, such efforts were in vain. Complexes **1–3** were isolated from MeOH/H₂O or MeCN/H₂O even employing a $M(O_2CMe)_2 \cdot 4H_2O / (2-py)_2CO$ ratio of 3:1. With the identities of **1–3** established, the “correct” stoichiometries, i.e. $Mn(O_2CMe)_2 \cdot 4H_2O / (2-py)_2CO / Na[N(CN)_2] = 1:1.5:0.5$ and $M(O_2CMe)_2 \cdot 4H_2O / (2-py)_2CO / Na[N(CN)_2] = 1:1:0.5$ (M = Co, Ni), were employed and led to pure **1** and **2** but not to pure **3** (vide infra). It is worth mentioning that (2-py)₂CO₂^{2−} complexes are known in M^{II}/(2-py)₂CO/N₃[−] chemistry.^[18b,18c] Since these complexes contain η¹:μ₄-azido ligands, the failure to isolate analogous dicyanamide complexes may be in part due to the inability of the N(CN)₂[−] anion to adopt an η¹:μ₄ ligation mode. Lastly, in the case of the cobalt reaction systems *only*, there is a second product. The chemical and structural identity of the product depends on the Co^{II}/(2-py)₂CO ratio, reaction time, temperature and solution concentration. Upon employing an excess of (2-py)₂CO, i.e. Co^{II}/(2-py)₂CO = 1:2, long reaction times, reflux conditions and high dilution (to avoid precipitation of the more insoluble tetranuclear Co^{II} cluster), slow oxidation of Co^{II} takes place under the normal laboratory atmosphere leading to the pure mononuclear complex [Co^{III}{(2-py)C(OH)O}₂]{N(CN)₂}₂·4H₂O (**4**) in very good yields (≈ 70%). The source of the oxidising agent is oxygen from the air, facilitated by the mild reducing nature of Co^{II} in a nitrogen-rich environment. It is likely, as with other reactions in Co chemistry, that the reaction solution contains a mixture of two or more species in equilibrium, with factors such as relative solubility, reaction ratio, lattice energy, crystallisation kinetics and other factors determining the identity of the isolated product. Somewhat to our surprise, an analogous Mn^{III} complex (or a mixed-valent Mn^{II/III} species) was not formed under the conditions employed.

Description of Structures

[Mn₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄]·2(2-py)₂CO·4H₂O (**1**)

A partially labelled plot of the tetranuclear molecule [Mn₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄] present in

compound **1** is shown in Figure 3. Selected interatomic distances and angles are listed in Table 1. The solvate (2-py)₂CO and H₂O molecules will not be further discussed.

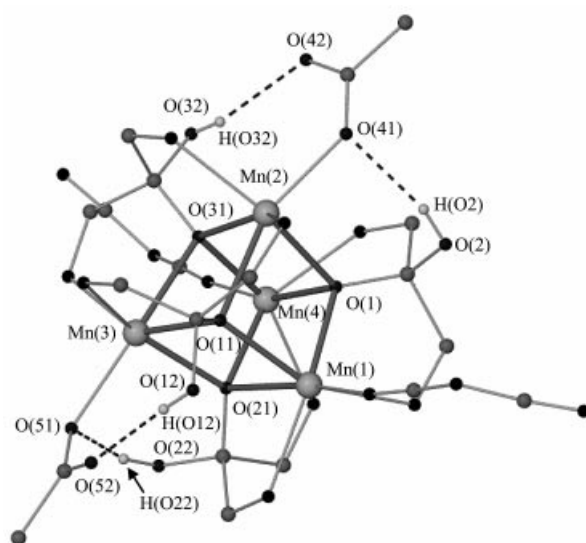


Figure 3. A partially labelled plot of the tetranuclear cluster molecule present in complex **1**. Many carbon atoms of the (2-py)₂C(OH)O[−] ligands have been omitted for clarity. The intracubane hydrogen bonds are also shown.

The tetranuclear cluster molecule of **1** has a cubane [Mn₄(μ₃-OR)₄]⁴⁺ core with Mn^{II} and oxygen atoms occupying alternate vertices. Thus, the molecule consists of two interpenetrating tetrahedra, one of four Mn^{II} atoms and one of four μ₃-oxygen atoms originating from the (2-py)₂C(OH)O[−] ligands. In addition to three μ₃ oxygen atoms, each Mn^{II} atom is coordinated to two N atoms belonging to two different (2-py)₂C(OH)O[−] ligands and a single anion to complete an octahedral coordination environment. For Mn(1) and Mn(4), the anion is a monodentate N(CN)₂[−] group bonded through a nitrile nitrogen atom, whereas a monodentate acetate ligand completes the sixth coordination position at Mn(2) and Mn(3). Thus, the chromophores are Mn(1,4)O₃N₃ and Mn(2,3)O₄N₂. One octahedral face of each Mn^{II} atom is occupied by the three alkoxide-type oxygen atoms and the other contains the remaining donor atoms.

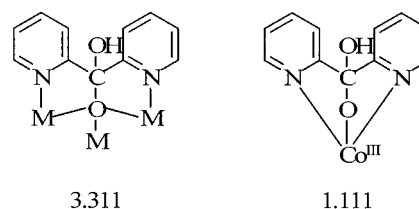
One oxygen atom of each (2-py)₂C(OH)O[−] remains protonated and unbound to the metal ions. The resultant monoanion functions as an η¹:η³:η¹:μ₃ ligand (or as a 3.311 ligand using the Harris notation^[25]) forming two five-membered MnNCCO chelating rings with two different metals (these rings share a common C–O edge) and an alkoxide-type bond to a third Mn^{II} atom (Figure 4). This ligation mode is common in the coordination chemistry of hydrated di-2-pyridyl ketone.^[14] The large number of ligands involved results in a structure devoid of any point-group symmetry elements.^[26]

There are two types for Mn–O (alkoxide-type) bonds for each metal ion: one bond is rather elongated to an average

Table 1. Selected interatomic distances [Å] and angles [°] for $[\text{Mn}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 2(2\text{-py})_2\text{CO}\cdot 4\text{H}_2\text{O}$ (1).

Mn(1)···Mn(2)	3.274(1)	Mn(3)–O(51)	2.137(3)
Mn(1)···Mn(3)	3.432(2)	Mn(3)–N(11)	2.223(3)
Mn(1)···Mn(4)	3.447(2)	Mn(3)–N(32)	2.271(3)
Mn(2)···Mn(3)	3.385(2)	Mn(4)–O(1)	2.308(3)
Mn(2)···Mn(4)	3.455(2)	Mn(4)–O(21)	2.170(3)
Mn(3)···Mn(4)	3.310(2)	Mn(4)–O(31)	2.186(3)
Mn(1)–O(1)	2.162(3)	Mn(4)–N(2)	2.213(4)
Mn(1)–O(11)	2.168(3)	Mn(4)–N(21)	2.276(4)
Mn(1)–O(21)	2.324(3)	Mn(4)–N(51)	2.171(4)
Mn(1)–N(1)	2.289(4)	C(92)–O(41)	1.274(5)
Mn(1)–N(22)	2.198(4)	C(92)–O(42)	1.237(5)
Mn(1)–N(41)	2.146(4)	C(94)–O(51)	1.269(5)
Mn(2)–O(1)	2.206(3)	C(94)–O(52)	1.227(6)
Mn(2)–O(11)	2.251(3)	N(43)–C(74)	1.123(8)
Mn(2)–O(31)	2.165(2)	N(42)–C(74)	1.294(8)
Mn(2)–O(41)	2.088(3)	C(73)–N(42)	1.284(7)
Mn(2)–N(12)	2.240(3)	N(41)–C(73)	1.133(6)
Mn(2)–N(31)	2.243(3)	C(76)–N(53)	1.115(8)
Mn(3)–O(11)	2.196(3)	N(52)–C(76)	1.281(8)
Mn(3)–O(21)	2.180(3)	N(52)–C(75)	1.284(6)
Mn(3)–O(31)	2.273(3)	C(75)–N(51)	1.135(6)
O(1)–Mn(1)–O(11)	83.3(1)	O(31)–Mn(3)–N(11)	100.8(1)
O(1)–Mn(1)–O(21)	78.7(1)	O(31)–Mn(3)–N(32)	70.6(1)
O(1)–Mn(1)–N(1)	72.1(1)	O(51)–Mn(3)–N(11)	97.9(1)
O(1)–Mn(1)–N(22)	146.2(1)	O(51)–Mn(3)–N(32)	91.9(1)
O(1)–Mn(1)–N(41)	111.2(1)	N(11)–Mn(3)–N(32)	96.9(1)
O(11)–Mn(1)–O(21)	77.0(1)	O(1)–Mn(3)–O(21)	78.9(1)
O(11)–Mn(1)–N(1)	155.2(1)	O(1)–Mn(3)–O(31)	75.9(1)
O(11)–Mn(1)–N(22)	106.4(1)	O(1)–Mn(4)–N(2)	72.4(1)
O(11)–Mn(1)–N(41)	98.1(1)	O(1)–Mn(4)–N(21)	99.9(1)
O(21)–Mn(1)–N(1)	100.9(1)	O(1)–Mn(4)–N(51)	164.8(1)
O(21)–Mn(1)–N(22)	72.4(1)	O(21)–Mn(4)–O(31)	81.7(1)
O(21)–Mn(1)–N(41)	168.6(1)	O(21)–Mn(4)–N(2)	146.3(1)
N(1)–Mn(1)–N(22)	96.2(1)	O(21)–Mn(4)–N(21)	72.3(1)
N(1)–Mn(1)–N(41)	87.9(1)	O(21)–Mn(4)–N(51)	115.0(1)
N(22)–Mn(1)–N(41)	99.6(1)	O(31)–Mn(4)–N(2)	107.4(1)
O(1)–Mn(2)–O(11)	80.4(1)	O(31)–Mn(4)–N(21)	154.0(1)
O(1)–Mn(2)–O(31)	78.5(1)	O(31)–Mn(4)–N(51)	99.2(1)
O(1)–Mn(2)–O(41)	89.0(1)	N(2)–Mn(4)–N(21)	95.3(1)
O(1)–Mn(2)–N(12)	112.4(1)	N(2)–Mn(4)–N(51)	95.9(1)
O(1)–Mn(2)–N(31)	150.9(1)	N(21)–Mn(4)–N(51)	90.8(1)
O(11)–Mn(2)–O(31)	80.4(1)	Mn(1)–O(1)–Mn(2)	97.1(1)
O(11)–Mn(2)–O(41)	154.8(1)	Mn(1)–O(1)–Mn(4)	100.9(1)
O(11)–Mn(2)–N(12)	72.5(1)	Mn(1)–O(11)–Mn(2)	95.6(1)
O(11)–Mn(2)–N(31)	103.1(1)	Mn(1)–O(11)–Mn(3)	103.7(1)
O(31)–Mn(2)–O(41)	120.0(1)	Mn(1)–O(21)–Mn(4)	100.1(1)
O(31)–Mn(2)–N(12)	148.0(1)	Mn(1)–O(21)–Mn(3)	99.2(1)
O(31)–Mn(2)–N(31)	73.8(1)	Mn(2)–O(1)–Mn(4)	99.8(1)
O(41)–Mn(2)–N(12)	91.0(1)	Mn(2)–O(11)–Mn(3)	99.1(1)
O(41)–Mn(2)–N(31)	97.3(1)	Mn(2)–O(31)–Mn(3)	99.4(1)
N(12)–Mn(2)–N(31)	95.9(1)	Mn(2)–O(31)–Mn(4)	105.1(1)
O(11)–Mn(3)–O(21)	79.5(1)	Mn(3)–O(21)–Mn(4)	99.1(1)
O(11)–Mn(3)–O(31)	79.3(1)	Mn(3)–O(31)–Mn(4)	95.8(1)
O(11)–Mn(3)–O(51)	121.3(1)	O(41)–C(92)–O(51)	124.4(4)
O(11)–Mn(3)–N(11)	73.1(1)	O(51)–C(94)–O(52)	125.6(4)
O(11)–Mn(3)–N(32)	146.1(1)	N(43)–C(74)–N(42)	171.0(8)
O(21)–Mn(3)–O(31)	79.5(1)	C(74)–N(42)–C(73)	122.7(6)
O(21)–Mn(3)–O(51)	91.1(1)	N(42)–C(73)–N(41)	171.7(6)
O(21)–Mn(3)–N(11)	151.9(1)	N(53)–C(76)–N(52)	171.2(7)
O(21)–Mn(3)–N(32)	109.4(1)	C(76)–N(52)–C(75)	127.0(5)
O(31)–Mn(3)–O(51)	155.8(1)	N(52)–C(75)–N(51)	172.2(6)

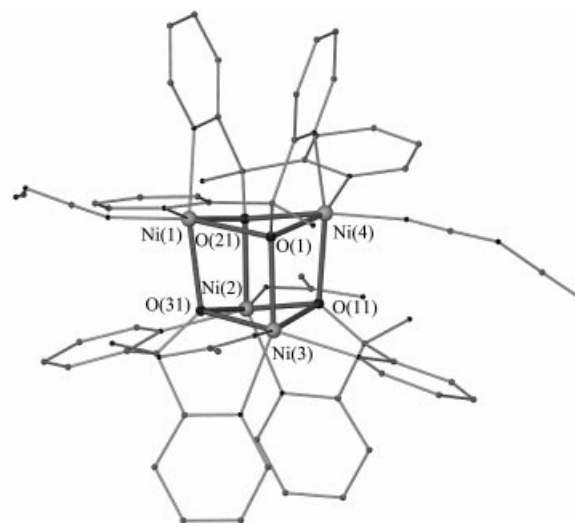
distance of 2.289 Å, whereas the two other bonds are shorter (average distance 2.179 Å). The cube deviates from the ideal geometry. The internal cube angles (RO–Mn–OR) at the metal vertices average 79.4°, whereas the comparable

Figure 4. The crystallographically established coordination modes of the ligand $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ present in complexes **1–4** and the Harris notation^[25] which describes these modes (M = Mn^{II}, Co^{II}, Ni^{II}).

angles at the alkoxide corners (Mn–OR–Mn) are much larger averaging 99.6°. The Mn···Mn vectors in the complex reflect the different Mn–O (alkoxide-type) bond lengths, with the two Mn(1)···Mn(2) and Mn(3)···Mn(4) [3.274(1) and 3.310(2), respectively] cube face diagonals being shorter than the four other face diagonal vectors [3.385(2)–3.455(2) Å]. The bond distances around the Mn^{II} atoms are typical of those found in octahedrally coordinated high-spin manganese(II) complexes with O- and N-ligation.^[16a,19d,27–29] A few Mn^{II} cubane structures containing $[\text{Mn}_4(\mu_3\text{-OR}_4)]^{4+}$ cores have been reported previously.^[16a,28,29]

$[\text{Ni}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 10\text{H}_2\text{O}$ (2)

A partially labelled plot of the tetranuclear molecule present in compound **2** is shown in Figure 5. Selected interatomic distances and angles are listed in Table 2. Complex **2** crystallises in the triclinic space group $P\bar{1}$. Its structure consists of the tetranuclear $[\text{Ni}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$ moiety and solvate H_2O molecules. The latter will not be further discussed.

Figure 5. Partially labelled representation of the tetranuclear cluster molecule present in complex **2** emphasising its cubane structure.

The molecular structure of $[\text{Ni}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$ is very similar to that of the tetranuclear cluster of complex **1**. Clearly, the replacement of Mn^{II} by Ni^{II} has little structural effect. The $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ core in **2** has almost all the geometric features found in the core of **1**, except that three Ni–O (alkoxide-type) distances are real-

Table 2. Selected interatomic distances [Å] and angles [°] for $[\text{Ni}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 10\text{H}_2\text{O}$ (**2**).

Ni(1)···Ni(2)	3.278(2)	Ni(3)–O(51)	2.039(4)
Ni(1)···Ni(3)	3.185(1)	Ni(3)–N(11)	2.068(4)
Ni(1)···Ni(4)	3.104(1)	Ni(3)–N(32)	2.076(5)
Ni(2)···Ni(3)	3.104(1)	Ni(4)–O(1)	2.018(3)
Ni(2)···Ni(4)	3.185(2)	Ni(4)–O(21)	2.150(3)
Ni(3)···Ni(4)	3.249(2)	Ni(4)–O(31)	2.094(3)
Ni(1)–O(1)	2.179(3)	Ni(4)–N(2)	2.122(4)
Ni(1)–O(11)	2.094(3)	Ni(4)–N(21)	2.019(4)
Ni(1)–O(21)	2.021(3)	Ni(4)–N(51)	2.026(5)
Ni(1)–N(1)	2.042(4)	C(81)–O(41)	1.264(6)
Ni(1)–N(22)	2.107(4)	C(81)–O(42)	1.255(7)
Ni(1)–N(41)	2.041(5)	C(91)–O(51)	1.264(7)
Ni(2)–O(1)	2.105(3)	C(91)–O(52)	1.252(8)
Ni(2)–O(11)	2.022(3)	N(43)–C(94)	1.148(9)
Ni(2)–O(31)	2.167(3)	C(94)–N(42)	1.323(10)
Ni(2)–O(41)	2.037(4)	N(42)–C(93)	1.309(8)
Ni(2)–N(12)	2.085(4)	C(93)–N(41)	1.137(7)
Ni(2)–N(31)	2.057(4)	N(53)–C(96)	1.152(13)
Ni(3)–O(11)	2.159(3)	C(96)–N(52)	1.304(13)
Ni(3)–O(21)	2.093(3)	N(52)–C(95)	1.301(8)
Ni(3)–O(31)	2.028(3)	C(95)–N(51)	1.130(7)
O(1)–Ni(1)–O(11)	75.6(1)	O(31)–Ni(3)–N(11)	156.5(2)
O(1)–Ni(1)–O(21)	82.0(1)	O(31)–Ni(3)–N(32)	78.3(2)
O(1)–Ni(1)–N(1)	77.3(2)	O(51)–Ni(3)–N(11)	91.6(2)
O(1)–Ni(1)–N(22)	104.8(1)	O(51)–Ni(3)–N(32)	92.4(2)
O(1)–Ni(1)–N(41)	169.3(2)	N(11)–Ni(3)–N(32)	96.8(2)
O(11)–Ni(1)–O(21)	81.5(1)	O(1)–Ni(4)–O(21)	82.8(1)
O(11)–Ni(1)–N(1)	103.7(2)	O(1)–Ni(4)–O(31)	82.2(1)
O(11)–Ni(1)–N(22)	158.3(2)	O(1)–Ni(4)–N(2)	77.1(2)
O(11)–Ni(1)–N(41)	95.3(2)	O(1)–Ni(4)–N(21)	158.0(2)
O(21)–Ni(1)–N(1)	156.5(2)	O(1)–Ni(4)–N(51)	102.9(2)
O(21)–Ni(1)–N(22)	77.2(2)	O(21)–Ni(4)–O(31)	76.6(1)
O(21)–Ni(1)–N(41)	102.5(2)	O(21)–Ni(4)–N(2)	102.9(1)
N(1)–Ni(1)–N(22)	97.5(2)	O(21)–Ni(4)–N(21)	77.9(1)
N(1)–Ni(1)–N(41)	99.2(2)	O(21)–Ni(4)–N(51)	169.0(2)
N(22)–Ni(1)–N(41)	85.7(2)	O(31)–Ni(4)–N(2)	159.1(2)
O(1)–Ni(2)–O(11)	78.8(1)	O(31)–Ni(4)–N(21)	103.2(2)
O(1)–Ni(2)–O(31)	78.5(1)	O(31)–Ni(4)–N(51)	94.7(2)
O(1)–Ni(2)–O(41)	88.7(1)	N(2)–Ni(4)–N(21)	97.0(2)
O(1)–Ni(2)–N(12)	156.2(1)	N(2)–Ni(4)–N(51)	87.6(2)
O(11)–Ni(2)–N(31)	107.9(2)	N(21)–Ni(4)–N(51)	97.9(2)
O(11)–Ni(2)–O(31)	82.3(1)	N(1)–O(1)–Ni(2)	99.8(1)
O(11)–Ni(2)–O(41)	112.2(1)	Ni(1)–O(1)–Ni(4)	95.3(1)
O(11)–Ni(2)–N(12)	78.3(1)	Ni(1)–O(11)–Ni(2)	105.6(1)
O(11)–Ni(2)–N(31)	156.1(2)	Ni(1)–O(11)–Ni(3)	97.0(1)
O(31)–Ni(2)–O(41)	158.7(1)	Ni(1)–O(21)–Ni(3)	101.5(1)
O(31)–Ni(2)–N(12)	104.3(1)	Ni(1)–O(21)–Ni(4)	96.1(1)
O(31)–Ni(2)–N(31)	76.9(2)	Ni(2)–O(1)–Ni(4)	101.1(1)
O(41)–Ni(2)–N(12)	94.3(2)	Ni(2)–O(11)–Ni(3)	95.8(1)
O(41)–Ni(2)–N(31)	91.2(2)	Ni(2)–O(31)–Ni(3)	95.4(1)
N(12)–Ni(2)–N(31)	95.6(2)	Ni(2)–O(31)–Ni(4)	96.7(1)
O(11)–Ni(3)–O(21)	78.3(1)	Ni(3)–O(21)–Ni(4)	99.9(1)
O(11)–Ni(3)–O(31)	82.3(1)	Ni(3)–O(31)–Ni(4)	104.0(2)
O(11)–Ni(3)–O(51)	160.1(2)	O(41)–C(81)–O(42)	123.0(5)
O(11)–Ni(3)–N(11)	76.6(1)	O(51)–C(91)–O(52)	125.1(6)
O(11)–Ni(3)–N(32)	104.8(2)	N(43)–C(94)–N(42)	172.4(8)
O(21)–Ni(3)–O(31)	79.3(1)	C(94)–N(42)–C(93)	121.7(6)
O(21)–Ni(3)–O(51)	90.0(2)	N(42)–C(93)–N(41)	172.0(6)
O(21)–Ni(3)–N(11)	106.3(2)	N(53)–C(96)–N(52)	172.3(1)
O(21)–Ni(3)–N(32)	156.7(1)	C(96)–N(52)–C(95)	121.7(8)
O(31)–Ni(3)–O(51)	111.5(1)	N(52)–C(95)–N(51)	173.2(8)

ised for each metal ion. One bond is short with an average distance of 2.022 Å, one bond is relatively long with an average distance of 2.164 Å, while the third bond is of intermediate strength (average Ni–O distance of 2.097 Å). As in

1, there are two chemically distinct metal sites in **2**. Two of them [Ni(1), Ni(4)] involve monodentate dicyanamides, while the other two [Ni(2), Ni(3)] are each bound to one monodentate acetate. The $\{\text{Ni}_4\text{O}_4\}$ cube also deviates from ideal geometry. The internal cube angles at the metal (OR–Ni–OR) average 80.0° whereas the analogous angles at the alkoxide-type corners (Ni–OR–Ni) are much larger averaging 99.0°. The Ni···Ni distances on opposite cubic faces are very similar, the pairs with the shortest distances being Ni(1)/Ni(4) and Ni(2)/Ni(3) (both distances are 3.104 Å). Average Ni–N and Ni–O bond lengths of 2.06 and 2.09 Å, respectively, lie well within the range of reported values for the corresponding bond lengths of other tetranuclear cubane Ni^{II} clusters.^[2e,12b,12d,16a,26,29–31]

Many $\{\text{Ni}_4\text{O}_4\}$ cubanes have been reported previously.^[2e,12b,12d,16a,26,29–31] Several^[2e,29,30] have simple μ_3 -alkoxides (CH_3O^- , $\text{C}_2\text{H}_5\text{O}^-$, ...) which provide the four oxygen centres. The first example which we were aware of involves terminal salicylaldehyde and ethanol ligands.^[30a] Since that date, terminal ligands attached to the $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ core have included acetylacetonate,^[30b] dibenzoylmethanate^[30c,30d] and 6-chloro-2-pyridonate.^[30e]

$[\text{Co}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 10\text{H}_2\text{O}$ (**3**)

As mentioned in the Experimental Section, the unit-cell determination along with IR and elemental analysis data proved that complex **3** is isostructural with **2**. A full data set was therefore not collected for the cobalt(II) cluster. Compound **3** is a new member of the family containing tetranuclear cobalt(II) cubanes with the $[\text{Co}_4(\mu_3\text{-OR})_4]^{4+}$ core.^[11b,15c,16a,29,31b,32]

Intracubane Hydrogen Bonding in **1** and **2**

There is a large amount of hydrogen bonding in **1** and **2**. We will briefly comment on the intracubane hydrogen bonds because they reinforce the framework of the cubes.^[28a] Details of these bonds are listed in Table 3. Each $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ hydroxyl group is strongly intramolecularly hydrogen bonded to an O atom from an acetate ligand. A notable feature here is that both uncoordinated and coordinated oxygen atoms of the terminal acetate ligands participate in one intracubane hydrogen bond. The intracubane

Table 3. Intracubane hydrogen bonding details for complexes **1** and **2**.^[a,b]

Complex	D–H···A	D···A [Å]	H···A [Å]	DHA [°]
1	O(2)–H(O2)···O(41) _c	2.756(1)	1.999(1)	161.5(1)
	O(12)–H(O12)···O(52)	2.704(1)	1.946(1)	177.2(1)
	O(22)–H(O22)···O(51) _c	2.801(2)	2.044(1)	154.6(1)
	O(32)–H(O32)···O(42)	2.842(1)	2.183(1)	167.6(1)
2	O(2)–H(O2)···O(41)	2.821(2)	2.190(1)	163.2(1)
	O(12)–H(O12)···O(42)	2.671(1)	1.955(1)	177.0(1)
	O(22)–H(O22)···O(51)	2.842(1)	2.168(1)	154.9(1)
	O(32)–H(O32)···O(52)	2.695(1)	2.044(1)	170.0(1)

[a] A = acceptor; D = donor. [b] The subscript c denotes a coordinated acetate oxygen.

hydrogen bonds have the effect of lowering the symmetry of the $[\text{M}_4(\mu_3\text{-OR})_4]^{4+}$ core.

Other $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ -Based Mn^{II} , Co^{II} and Ni^{II} Cubanes

Although several $(2\text{-py})\text{C}(\text{OH})\text{O}^-$ -based, tetranuclear Mn^{II} , Co^{II} and Ni^{II} clusters have been reported,^[14] only few have cubane structures in which the four μ_3 -oxygen atoms originate from four deprotonated ligands. This group of compounds currently includes $[\text{Co}_4(\text{O}_2\text{CMe})_4\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$,^[15c] $[\text{Mn}_4\text{Cl}_4\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$,^[16a] $[\text{Mn}_4(\text{O}_2\text{CMe})_3(\text{H}_2\text{O})\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4](\text{ClO}_4)$,^[16a] $[\text{Co}_4(\text{O}_2\text{CMe})_3(\text{H}_2\text{O})\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4](\text{ClO}_4)$,^[16a] $[\text{Ni}_4(\text{O}_2\text{CMe})_3(\text{H}_2\text{O})\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4](\text{ClO}_4)$ ^[16a] as well as **1**, **2** and **3**.

General Information on the Cubane 3d-Metal Clusters

The arrangement of four metal ions and four bridging ligands at alternating corners of a cube is a well-precedented unit in inorganic chemistry.^[28d] There is great interest in the synthesis and study of cubanes featuring the first-row transition-metals.^[30c,31b] Among the most thoroughly studied members of this class are $\{\text{Fe}_4\text{S}_4\}^{n+}$ clusters, many of which were prepared and characterised as models for the active site of iron-sulfur proteins.^[33] Later, following the proposal of a cubic arrangement of Mn ions and bridging ligands for the oxygen evolving centre (OEC) of photosystem II (PS II),^[34] several $\{\text{Mn}_4\text{X}_4\}^{n+}$ complexes with bridging oxo, chloro or alkoxo ligands were synthesised as models for this postulated unit.^[35] More recently,^[36] crystallographic data for a cyanobacterial PS II complex at 3.5 Å resolution strongly suggested that the OEC contains a cubane-like $\{\text{Mn}_3\text{CaO}_4\}$ cluster linked to a fourth Mn by a mono- μ -oxo bridge. However, higher resolution data are required to investigate whether some of the bridging oxygen atoms are protonated. It has also been suggested^[31b,37] that these cubanes offer a way to model, and so better understand, the properties of extended networks which are often based on a cubane repeat unit.

$[\text{Co}\{(2\text{-py})\text{C}(\text{OH})\text{O}\}_2]\{\text{N}(\text{CN})_2\}\cdot 4\text{H}_2\text{O}$ (**4**)

A labelled plot of the structure of the mononuclear cation $[\text{Co}\{(2\text{-py})\text{C}(\text{OH})\text{O}\}_2]^+$ present in complex **4** is shown in Figure 6. Selected bond lengths, angles and hydrogen bonding details are listed in Table 4 and Table 5, respectively. The structure consists of the above mentioned mononuclear cation, one disordered $\text{N}(\text{CN})_2^-$ anion and H_2O solvate molecules; the latter two will not be further discussed. The Co^{III} ion sits on a crystallographic inversion centre.

The geometry of the *trans*- $\text{Co}^{\text{III}}\text{N}_4\text{O}_2$ chromophore is nearly octahedral, as would be expected for a Co^{III} species, with the $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ anions adopting the tridentate chelating coordination mode $\eta^1:\eta^1:\eta^1$ (or, 1.111 using Harris notation^[25]) shown in Figure 4. The angle subtended by the off-axis coordination of the oxygen atom [O(1)] with the line normal to the equatorial N_4 plane is very small, with a value of 13.8°. The Co–O and Co–N bond lengths agree well with values expected for low-spin Co^{III} in octahedral

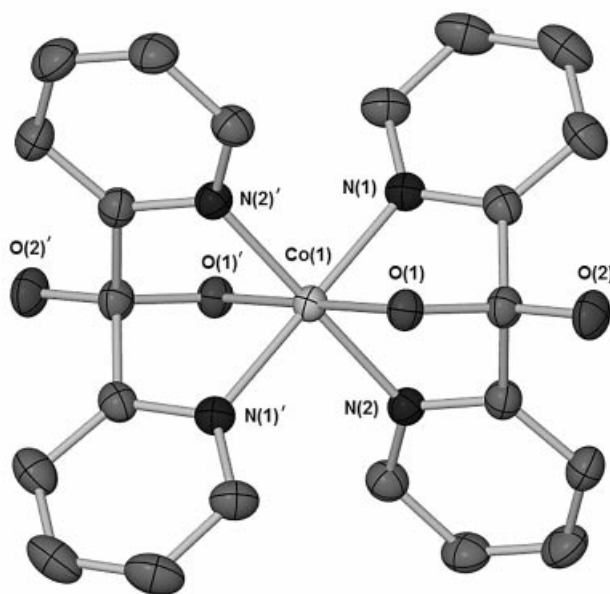


Figure 6. Partially labelled ORTEP plot of the mononuclear cation present in complex **4** with thermal ellipsoids at the 40% probability level. The primed atoms are related to the nonprimed ones by the crystallographic inversion centre.

Table 4. Selected bond lengths [Å] and angles [°] for $[\text{Co}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_2]\{\text{N}(\text{CN})_2\}\cdot 4\text{H}_2\text{O}$ (**4**).^[a]

Co(1)–O(1)	1.887(2)	C(6)–O(1)	1.400(3)
Co(1)–N(1)	1.922(2)	C(6)–O(2)	1.376(3)
Co(1)–N(2)	1.915(2)		
O(1)–Co(1)–N(1)	82.84(7)	N(1)–Co(1)–N(2)	88.69(9)
O(1)–Co(1)–N(2)	83.31(8)	N(1)–Co(1)–N(2')	91.32(9)
O(1)–Co(1)–N(1')	97.16(7)	O(1)–C(6)–O(2)	114.0(2)
O(1)–Co(1)–N(2')	96.69(8)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $-x, 1-y, 1-z$.

Table 5. Hydrogen bonding details for complex $[\text{Co}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_2]\{\text{N}(\text{CN})_2\}\cdot 4\text{H}_2\text{O}$ (**4**).^[a,b]

D–H...A	D...A [Å]	H...A [Å]	DHA [°]	Symmetry operator of A
O(2)–H(2A)...O(3)	2.669(3)	1.854	172.1	$x, y-1, z$
O(3)–H(31)...O(1)	2.730(3)	1.927	172.1	$-x, -y+1, -z+1$
O(3)–H(32)...O(4)	2.949(9)	2.136	170.2	$x-1, y+1, z$
O(4)–H(41)...N(11)	2.904(1)	2.062	179.3	$-x+1, -y+1, -z+2$
O(4)–H(42)...N(15)	2.903(1)	2.089	178.4	$-x+1, -y, -z+2$

[a] A = acceptor; D = donor. [b] Atoms O(3) and O(4) [not shown in Figure 6] belong to lattice water molecules, while N(11) and N(15) belong to the $\text{N}(\text{CN})_2^-$ counterion. Only the highest occupancy atoms appear.

environments.^[17b] There is a hydrogen bonding network among the H_2O molecules, the $\text{N}(\text{CN})_2^-$ counterion and both protonated and deprotonated hydroxyl groups of $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ leading to a 2D assembly (Figure 7).

The structure of the cation of **4**, as detailed in the short discussion above and in Table 4, shows remarkable similar-

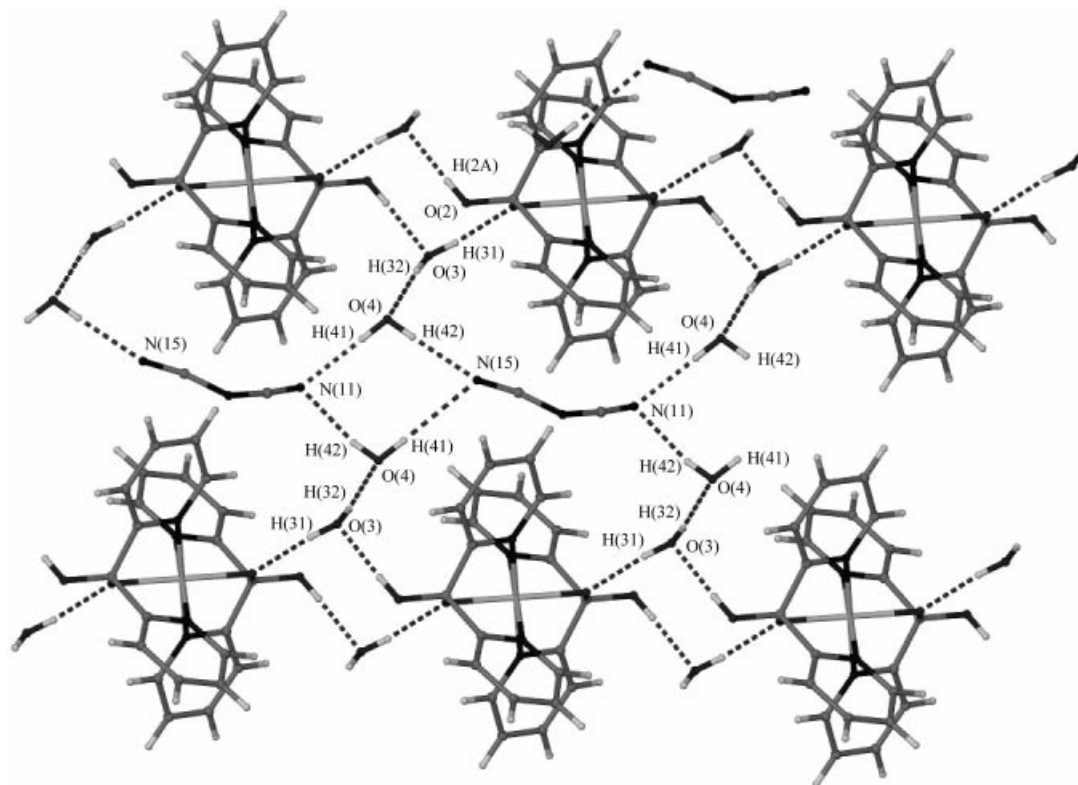


Figure 7. A view of the 2D network formed by hydrogen bonding in complex $[\text{Co}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_2][\text{N}(\text{CN})_2]\cdot 4\text{H}_2\text{O}$ (**4**).

ity to the structures of the cations in $[\text{Co}\{(2\text{-py})\text{-C}(\text{OH})\text{O}\}_2](\text{NO}_3)\cdot 2\text{H}_2\text{O}$,^[38a] $[\text{Co}\{(2\text{-py})\text{C}(\text{OH})\text{O}\}_2](\text{ClO}_4)\cdot 3\text{H}_2\text{O}$ ^[38b] and $[\text{Co}\{(2\text{-py})\text{C}(\text{OH})\text{O}\}_2](\text{MeO})\cdot \text{MeOH}$.^[38c] The latter was obtained from a reaction involving the oxidative degradation of bis[di(2-pyridyl)ethyl]amine in the presence of Co^{II} .

IR Spectra

Complexes **1** and **4** exhibit medium to strong intensity IR bands at 3419 (**1**) and 3500 (**4**) cm^{-1} , and 3329 (**1**) and ca. 3440 (**4**) cm^{-1} , assignable to $\nu(\text{OH})$ vibrations for the $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ and H_2O groups, respectively.^[15e] The broadness and relatively low frequencies of these bands are both indicative of hydrogen bonding. These two modes coincide at ca. 3450 cm^{-1} in the spectra of the isostructural compounds **2** and **3**.

The spectrum of **1** shows a medium band at 1685 cm^{-1} , suggesting that a certain amount of the organic ligand is present in its ketone form.^[17e] This mode is situated at the same wavenumber (1684 cm^{-1}) in the spectrum of free $(2\text{-py})_2\text{CO}$, confirming the nonparticipation of the ketone group in the coordination in complex **1**. The spectra of **2–4** do not exhibit bands in the region expected for $\nu(\text{C}=\text{O})$ absorptions, with the nearest strong IR absorptions at 1602 (**2, 3**) and 1610 (**4**) cm^{-1} which can be assigned as 2-pyridyl stretching modes raised from 1582 cm^{-1} on coordination, as observed earlier^[15e,19d] upon complex formation involving

hydration of di-2-pyridyl ketone. The strong and rather broad band at 1602 cm^{-1} in **2** and **3** has $\nu_{\text{as}}(\text{CO}_2)$ character^[39] since no other strong band can be observed in the 1600–1515 cm^{-1} region. The $\nu_{\text{s}}(\text{CO}_2)$ modes are difficult to assign due to the presence of 2-pyridyl stretching bands at 1440–1415 cm^{-1} and, thus, the application of the spectroscopic criterion of Deacon and Phillips^[39] is extremely difficult.

The dicyanamide free anion in $\text{Na}[\text{N}(\text{CN})_2]$ shows three sharp and medium to strong characteristic stretching bands in the 2290 to 2170 cm^{-1} region attributable to a $\nu_{\text{as}}(\text{C}-\text{N}) + \nu_{\text{s}}(\text{C}-\text{N})$ combination mode (2286 cm^{-1}), $\nu_{\text{as}}(\text{C}\equiv\text{N})$ (2232 cm^{-1}) and $\nu_{\text{s}}(\text{C}\equiv\text{N})$ (2179 cm^{-1}).^[22d] Monodentate coordination has been reported to have a minor effect on these features, whereas the bridging modes of $\text{N}(\text{CN})_2^-$ cause a displacement of these bands towards higher frequencies, the effect increasing as one goes from bidentate to tridentate bonding.^[22a] In compounds **1–3** the three bands occur at 2270–2279, 2210–2231 and 2156–2164 cm^{-1} . These features are indicative of terminal monodentate coordination and are consistent with the X-ray structures of **1** and **2** where $\text{N}(\text{CN})_2^-$ was found to coordinate to the metal ions through one of its cyano nitrogen atoms. The $\nu_{\text{as}}(\text{C}-\text{N}) + \nu_{\text{s}}(\text{C}-\text{N})$ (2275 cm^{-1}), $\nu_{\text{as}}(\text{C}\equiv\text{N})$ (2238 cm^{-1}) and $\nu_{\text{s}}(\text{C}\equiv\text{N})$ (2191 cm^{-1}) vibrations of **4** appear almost at the same frequencies as the corresponding ones in $\text{Na}[\text{N}(\text{CN})_2]$, confirming the ionic nature of dicyanamide in the Co^{III} complex. The bands at ca. 1350 and 900–950 cm^{-1} in the spectra of **1–4** can be assigned to the $\nu_{\text{as}}(\text{C}-\text{N})$ and

$\nu_s(\text{C-N})$ vibrations, respectively, with a satisfactory degree of certainty.^[22a,22g,22i]

Magnetic Studies

Solid-state dc magnetic-susceptibility measurements were performed on polycrystalline samples of **1–3** in a 0.1 T field in the range 2.0–300 K. The $\chi_M T$ vs. T and χ_M vs. T plots for **1** are shown in Figure 8. The $\chi_M T$ value is 18.6 cm³ mol^{−1} K at room temperature, close to the expected value of 17.5 cm³ mol^{−1} K for four $S = 5/2$ uncoupled spins with $g = 2$. The $\chi_M T$ value decreases slightly in the 300–40 K range and then decreases sharply, reaching a value of 1.0 cm³ mol^{−1} K at 2.0 K, whereas a maximum of 0.649 cm³ mol^{−1} in the χ_M vs. T plot is observed at 9 K. The data suggest that the complex appears to possess intramolecular antiferromagnetic interactions. Inspection of the molecular structure (Table 1) reveals that the Mn–O–Mn bond angles in the six faces of the cube are all different. However, if we divide the six faces into three pairs of opposite faces, each member of a given pair has a similar mean Mn–O–Mn bond angle with the other member of the same pair. Thus, the mean Mn–O–Mn bond angles for the faces Mn(1)O(1)Mn(2)O(11), Mn(3)O(21)Mn(4)O(31), Mn(1)O(11)Mn(3)O(21), Mn(2)O(1)Mn(4)O(31), Mn(1)O(1)Mn(4)O(21) and Mn(2)O(11)Mn(3)O(31) are 96.4, 97.5, 101.5, 102.5, 100.5 and 99.3°, respectively. Due to similarities of the mean Mn–O–Mn angles in opposite faces of the cubane motif, the experimental data were fitted using the expression derived from the isotropic Heisenberg Hamiltonian given by Equation (2). The fit of the scheme shown in Figure 9 was performed on χ_M vs. T data by means of the computer program CLUMAG which uses the irreducible tensor operator formalism (ITO).^[40] The best fit parameters were $J_1 = -1.71$ cm^{−1}, $J_2 = -0.81$ cm^{−1}, $J_3 = -0.27$ cm^{−1} and $g = 2.10$.

$$H = -J_1(S_1S_4 + S_2S_3) - J_2(S_1S_2 + S_3S_4) - J_3(S_1S_3 + S_2S_4) \quad (2)$$

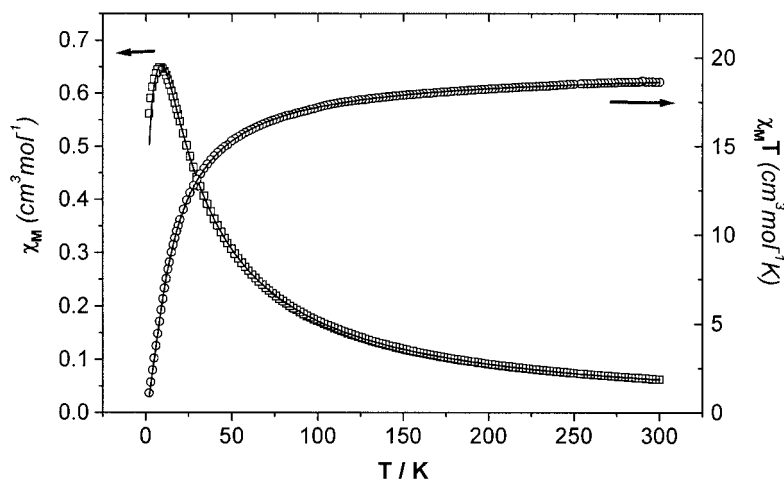


Figure 8. $\chi_M T$ vs. T and χ_M vs. T plots for complex **1**. The solid lines represent the best fit to the data as described in the text.

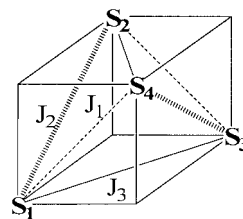


Figure 9. Assignments of J values to $M \cdots M$ interactions for the magnetic model with three coupling constants used for complexes **1** and **2** ($M = \text{Mn, Ni}$).

The J values of **1** are well within the narrow antiferromagnetic range (-0.22 to -4.11 cm^{−1}) reported for other cubane complexes containing the $[\text{Mn}_4(\mu_3\text{-OR})_4]^{4+}$ core.^[16a,28a,29]

The $\chi_M T$ vs. T and χ_M vs. T plots for **2** are shown in Figure 10. The $\chi_M T$ value at 300 K is 5.70 cm³ mol^{−1} K. As the temperature is lowered, $\chi_M T$ experiences a very slight increase, reaching a maximum value of 5.79 cm³ mol^{−1} K at 50 K followed by a much sharper decline at lower temperatures down to 0.84 cm³ mol^{−1} K at 2 K. On lowering the temperature, χ_M increases without a maximum to a value of 0.42 cm³ mol^{−1} at 2 K. The overall behaviour of **2** seems to have a ferromagnetic component. The structural parameters of **2** strongly suggest a lower symmetry than T_d for the molecule. As in compound **1**, if we divide the faces of the cube into three pairs of opposite faces, each face of a given pair has a similar mean Ni–O–Ni bond angle with the other member of the same pair. Thus, the mean Ni–O–Ni bond angles for the faces Ni(1)O(1)Ni(2)O(11), Ni(3)O(21)Ni(4)O(31), Ni(1)O(11)Ni(3)O(21), Ni(2)O(1)Ni(4)O(31), Ni(2)O(11)Ni(3)O(31) and Ni(1)O(1)Ni(4)O(21) are 102.7, 102.0, 99.3, 98.9, 95.6 and 95.7°, respectively. Again, as in **1**, the experimental data were fit using the expression derived from the isotropic Heisenberg Hamiltonian given by Equation (2). The fit on the scheme of Figure 9 was performed on $\chi_M T$ vs. T data by means of the computer program CLUMAG.^[40] The best fit parameters were $J_1 = 8.63$ cm^{−1}, $J_2 = -4.43$ cm^{−1}, $J_3 = -0.53$ cm^{−1} and $g = 2.10$.

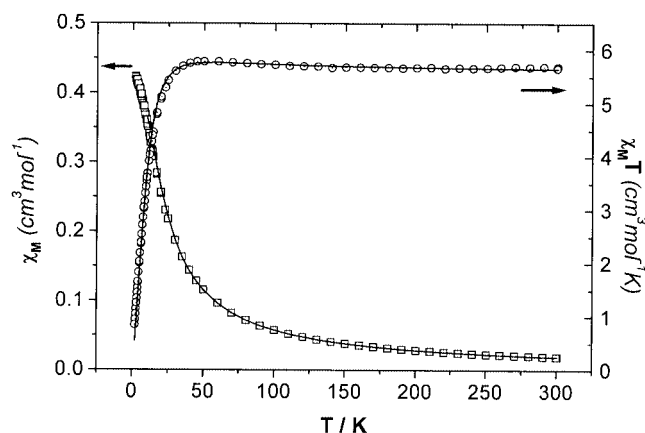


Figure 10. $\chi_M T$ vs. T and χ_M vs. T plots for complex **2**. The solid line represents the best theoretical fit of the data (see text for details).

It should be stressed at this point that the most important parameter in the magnetostructural correlation of tetranuclear nickel(II) complexes possessing the $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ cubane core has been reported^[2e,26,29,30c,31a,41] to be the average Ni–O–Ni angle of a cubane face. A ferromagnetic exchange interaction can be observed for Ni–O–Ni angles lower than 99° and the J value increases as the angle decreases. On the other hand, Ni–O–Ni angles in the vicinity of, and larger than, 99° lead to an antiferromagnetic interaction and the $|J|$ value increases as the angle increases. Accordingly, a linear correlation between J and the Ni–O–Ni angle has been reported.^[30c] The differences in sign and in absolute values among the J_1 , J_2 and J_3 superexchange interactions are in good agreement with the three different types of faces present in the cubane core of **2** and support the 3- J model used which takes into account the reduced symmetry of the core observed in the X-ray structure of the complex. In **2**, the average Ni–O–Ni angles in the three different sets of faces are 102.4 , 99.1 and 95.7° . Thus, the ferromagnetic coupling $J_1 = 8.63 \text{ cm}^{-1}$ should be associated

with the faces $[\text{Ni}(2)\text{O}(11)\text{Ni}(3)\text{O}(31)$, $\text{Ni}(1)\text{O}(1)\text{Ni}(4)\text{O}(21)]$ characterised by the mean angle of 95.7° . The J_2 value of -4.43 cm^{-1} can be assigned to the faces $[\text{Ni}(1)\text{O}(1)\text{Ni}(2)\text{O}(11)$, $\text{Ni}(3)\text{O}(21)\text{Ni}(4)\text{O}(31)]$ with the mean angle of 102.4° , while the very weak antiferromagnetic coupling $J_3 = -0.53 \text{ cm}^{-1}$ should be assigned to the remaining two faces with the mean angle of 99.1° . The variable-temperature magnetic susceptibilities for most cubane Ni^{II} complexes have been interpreted on the basis of 1- J or 2- J models.^[16a,29,30c,31b] Since the magnetic properties of only few $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ cubanes have necessitated a 3- J interpretation, Table 6 conveniently summarises some recent members of this small family.

The $\chi_M T$ vs. T plot for **3** is shown in Figure 11. The tetranuclear cluster exhibits a $\chi_M T$ value of $11.85 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K which is higher than the spin-only value expected ($7.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for four uncoupled Co^{II} centres in the 4T_1 ground state ($S = 3/2$) with $g = 2$. One reason for this is that the orbital degeneracy of this state is not quenched and, consequently, there is a significant orbital contribution to the magnetic moment.^[31b] As the temperature is lowered, $\chi_M T$ slightly increases to reach a broad maximum of $12.35 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 45 K , then decreases reaching a local minimum at about 25 K and below this temperature it sharply increases to a maximum value of $13.67 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 6 K , before dropping sharply to $11.58 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K . χ_M increases continuously upon cooling from a value of $0.0395 \text{ cm}^3 \text{ mol}^{-1}$ at room temperature to a value of $5.79 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K . The overall behaviour of **3** indicates a moderately weak ferromagnetic interaction. The shape of the $\chi_M T$ vs. T plot is probably due to the mixing of phenomena such as the ferromagnetic interaction with the depopulation of the $S = 3/2$ spin levels due to zero-field splitting. The uncommon shape of the $\chi_M T$ vs. T plot is quite reproducible and was confirmed by measurements on different samples (microcrystalline powder, ground crystals, different batches). Analysis of the coupling constants for a high-spin rhombic cobalt(II) tetramer is not possible by me-

Table 6. J [cm^{-1}] as a function of the mean Ni–O–Ni angles [$^\circ$] for selected $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ -type cubanes the magnetic interpretation of which necessitated the employment of 3- J models.^[a]

Complex ^[b]	mean Ni–O–Ni	J	Ref.
$[\text{Ni}_4(\mu_3\text{-OH})_2(\text{pyentO})(\text{O}_2\text{CMe})_2(\text{pym})(\text{NCS})_2(\text{H}_2\text{O})]$	89.9	15.0	[26]
	92.9	6.7	
	100.5	−3.1	
$[\text{Ni}_4(\mu_3\text{-OMe})_2(\text{LH})_2(\text{O}_2\text{CMe})_2(\text{MeOH})_2]$	95.9	8.0	[31a]
	97.9	0.9	
	99.0	−3.9	
$[\text{Ni}_4(\mu_3\text{-OMe})_4(\text{L}^{\text{Se}})_2(\text{MeOH})_2(\text{MeCN})_2]$	96.2	5.5	[2e]
	97.2	1.0	
	101.3	−4.1	
$[\text{Ni}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$	95.7	8.6	this work
	99.1	−0.5	
	102.4	−4.4	

[a] The 3- J models employed are not necessarily the same. [b] LH = the dianion of a Schiff base ligand derived from the [1+2] condensation of 2,6-diformyl-4-methylphenol and 6-amino-2,4-di-*tert*-butylphenol. L^{Se} = the dianion of 2,2'-selenobis(4,6-di-*tert*-butylphenol). Pym = the monoanion of 2-pyridylmethanol. PyentO = the monoanion of 1,5-bis[(2-pyridylmethyl)amino]pentan-3-ol.

ans of an effective Hamiltonian based on four $S = 3/2$ spins due to the large anisotropy of this ion.^[19c,19d,29] Thus, several measurements were performed in order to characterise the ground state and the sign of the dominant interactions. To rule out any kind of long-range ordering phenomena, ac susceptibility measurements were performed. No out-of-phase response was obtained and dc susceptibility data were also collected under variable external fields (0.3, 0.1 and 0.02 T). The measurements revealed that the low temperature $\chi_M T$ values are field independent indicating a strictly molecular response. Magnetisation experiments show an increase of magnetisation at low fields (M is 6 in $N\beta$ units at 1 T), reaching an $N\beta$ value of 8.3 under the maximum external field of 5 T and clearly indicating a ferromagnetic interaction. Finally, the EPR spectrum of **3** at 4 K shows the typical transition between the $\pm 2 m_s$ levels at low fields ($g = 15.5$).

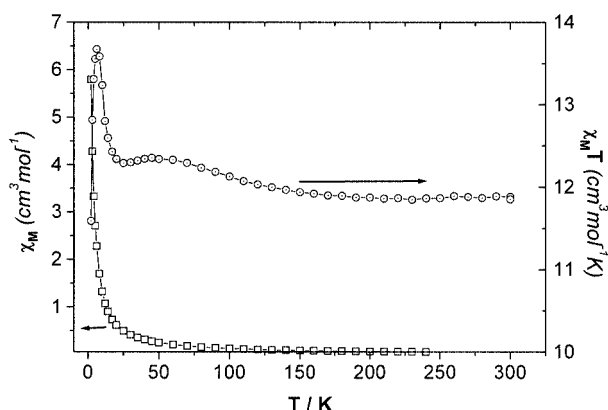


Figure 11. $\chi_M T$ (open circles) vs. T and χ_M (open squares) vs. T plot for complex **3**.

Based on the above data, the ground state of compound **3** can be adequately described as an effective, largely anisotropic, $S' = 2$ system, obtained from the ferromagnetic coupling of the four low-temperature local spins of the four Co^{II} ($S = 1/2$) ions. Complex **3** joins a handful of ferromagnetically coupled tetranuclear complexes consisting of a cubane $[\text{Co}_4(\mu_3\text{-OR})_4]^{4+}$ core.^[11b,15c,16a,29,42]

Conclusion and Perspectives

The first use of the dicyanamido ligand in manganese(II), cobalt(II) and nickel(II) acetate chemistry of $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, i.e. the study of the coordination chemistry of the $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-/\text{MeCO}_2^-/\text{N}(\text{CN})_2^-$ “ternary ligand blend” has provided access to three new neutral cubane clusters and one mononuclear Co^{III} complex. The three $\{\text{M}_4(\text{OR})_4\}$ cubes described are valuable additions to the chemistry of tetranuclear Mn^{II} , Co^{II} and Ni^{II} clusters. With the characterisation of **1–3**, the cubane geometry known for the 3d-metal/ $\text{RCO}_2^-/(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ systems can now be considered a feature of 3d-metal/ $\text{RCO}_2^-/\text{pseudohalide}/(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ chemistry as well. Complexes **1–3** contain low-symmetry cubane cores with different $\text{M}\cdots\text{M}$ distances and

M–O–M angles, resulting in three types of $\{\text{M}_2\text{O}_2\}$ faces. The lower symmetry of the cubanes has necessitated the use of three discrete exchange parameters for the interpretation of the magnetic properties of **1** and **2**, a fact which is rare in the magnetochemical literature of 3d-metal cubanes. For Ni^{II} , it has recently been emphasised by Chaudhuri, Wieghardt and coworkers^[31a] that other structural parameters such as $\text{Ni}\cdots\text{Ni}$ and $\text{Ni}\cdots\text{O}$ distances may be important in the magnetostructural correlation for the low-symmetry $[\text{Ni}_4(\mu_3\text{-OR})_4]^{4+}$ cubane core. Thus, more such distorted cubane-type Ni^{II} complexes are needed to resolve this open question.

Analogues of compounds **1–3** with other pseudohalides, e.g. N_3^- and NCO^- , are not known, at least to date, and it is currently not evident whether the preparation and stability of these Mn^{II} , Co^{II} and Ni^{II} cubanes are dependent on the particular nature of the pseudohalide ligand. Work is in progress to clarify this matter. The dicyanamido and/or acetate terminal ligands present in **1–3** could have future utility as sites for facile incorporation of other monodentate ligands by metathesis or as a means of accessing higher-nuclearity cationic species by using bis(monodentate) bridging aromatic heterocycles. Finally, since the intended bridging behaviour of $\text{N}(\text{CN})_2^-$ has not been achieved in **1–3**, we are intensively continuing our synthetic efforts to realise the bridging ($\mu_2\text{-}\mu_5$) potential of $\text{N}(\text{CN})_2^-$ in the 3d-metal carboxylate/di-2-pyridyl ketone chemistry.

Experimental Section

Materials and Physical Measurements: All manipulations were performed under aerobic conditions using reagents and solvents (Merck, Aldrich) as received. Elemental analyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Service using an EA 108 Carlo–Erba analyser. IR spectra ($400\text{--}450\text{ cm}^{-1}$) were recorded in KBr pellets on Nicolet 520 and Perkin–Elmer PC 16 FTIR spectrometers. Magnetic susceptibility measurements under magnetic fields of approximately 0.1 T in the range $2\text{--}300\text{ K}$ and magnetisation measurements (only for complex **3**) in the field range of $1\text{--}5\text{ T}$ were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were performed on polycrystalline samples. Pascal’s constants were used to estimate the diamagnetic corrections which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities. EPR spectra were recorded on a Bruker ES200 spectrometer at X-band frequency.

$[\text{Mn}_4(\text{O}_2\text{CMe})_2\{\text{N}(\text{CN})_2\}_2\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]\cdot 2(2\text{-py})_2\text{CO}\cdot 4\text{H}_2\text{O}$ (1**):** A solution of $(2\text{-py})_2\text{CO}$ (0.099 g, 0.54 mmol) in MeOH (5 mL) was added to a stirred pale yellow aqueous solution (25 mL) of $\text{Mn}(\text{O}_2\text{CMe})_2\cdot 4\text{H}_2\text{O}$ (0.270 g, 1.10 mmol) and $\text{Na}[\text{N}(\text{CN})_2]$ (0.049 g, 0.55 mmol). The resultant yellow solution was stirred for about 10 min and was then allowed to slowly become more concentrated by evaporation at room temperature for a period of 10 days. Well-formed yellow crystals appeared which were collected by filtration, washed with MeOH (5 mL), Et_2O (3 mL) and dried in air. Yield (based on di-2-pyridyl ketone): 0.085 g (55%). $\text{C}_{74}\text{H}_{66}\text{Mn}_4\text{N}_{18}\text{O}_{18}$ (1715.21): calcd. C 51.8, H 3.9, N 14.7; found C 53.3, H 3.8, N 14.6. IR data (KBr pellet): $\tilde{\nu} = 3419$ (s), 3329 (s, broad), 3070 (w), 2926 (w), 2270 (m), 2210 (m), 2156 (s), 1685 (m),

1635 (w), 1600 (s), 1583 (s), 1474 (m), 1435 (m), 1386 (m), 1346 (m), 1320 (m), 1295 (w), 1247 (w), 1222 (m), 1155 (w), 1111 (m), 1080 (s), 1056 (s), 1016 (m), 995 (w), 946 (m), 908 (w), 828 (w), 804 (w), 781 (m), 751 (m), 694 (w), 678 (m), 663 (w), 652 (w), 638 (w), 616 (w), 589 (w), 524 (w), 484 (w), 453 (w) cm^{-1} .

[Ni₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄}]·10H₂O (2): This complex was prepared in a manner completely similar to complex **1** but using Ni(O₂CMe)₂·4H₂O (0.269 g, 1.08 mmol) in place of Mn(O₂CMe)₂·4H₂O. Green crystals of the product were isolated. Yield (based on di-2-pyridyl ketone): 0.099 g (50%). C₅₂H₆₂Ni₄N₁₄O₂₂ (1470.00): calcd. C 42.5, H 4.3, N 13.3; found C 42.4, H 4.3, N 13.4. IR data (KBr pellet): $\tilde{\nu}$ = 3448 (s, broad), 2859 (w), 2279 (m), 2231 (m), 2164 (s), 1602 (s), 1511 (w), 1472 (m), 1438 (m), 1418 (m), 1338 (m), 1292 (w), 1260 (w), 1223 (m), 1157 (w), 1123 (m), 1086 (s), 1062 (m), 1048 (m), 1023 (m), 952 (w), 904 (w), 804 (w), 775 (m), 764 (m), 683 (m), 658 (m), 642 (m), 595 (w), 520 (m), 479 (w) cm^{-1} .

[Co₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄}]·10H₂O (3): A solution of (2-py)₂CO (0.099 g, 0.54 mmol) in MeOH (4 mL) was added to a stirred pink aqueous solution (20 mL) of Co(O₂CMe)₂·4H₂O (0.269 g, 1.08 mmol) and Na[N(CN)₂] (0.049 g, 0.55 mmol). The resultant red solution was allowed to slowly concentrate at room temperature for a period of 2 days only. X-ray quality reddish-pink crystals formed which were collected by filtration, washed with cold MeOH (3 mL), Et₂O (3 mL) and dried in air. Yield (based on di-2-pyridyl ketone): 0.069 g (35%). C₅₂H₆₂Co₄N₁₄O₂₂ (1471.00): calcd. C 42.5, H 4.3, N 13.3; found C 42.6, H 4.2, N 13.3. IR data

(KBr pellet): $\tilde{\nu}$ = 3448 (s, broad), 2858 (w), 2279 (m), 2223 (m), 2162 (s), 1602 (s), 1511 (m), 1472 (m), 1436 (m), 1352 (m), 1338 (m), 1292 (w), 1260 (w), 1218 (m), 1157 (w), 1115 (m), 1093 (s), 1065 (m), 1045 (m), 1027 (m), 991 (m), 952 (w), 904 (w), 804 (w), 793 (m), 774 (m), 762 (m), 686 (m), 658 (m), 642 (m), 595 (w), 520 (m), 479 (w) cm^{-1} . In an attempt to obtain a second crop of the reddish-pink crystals of **3** (and thus to increase the yield), the filtrate obtained after separation of **3** was again allowed to slowly become more concentrated at room temperature. A gradual colour change to orange occurred over the course of 2–3 days. After several days reddish-pink and orange crystals were formed. They were carefully collected by filtration and rinsed with a small amount of cold MeOH. The two products were readily separable manually and the reddish-pink and orange crystals proved to be **3** and [Co^{III}{(2-py)₂C(OH)O}₂]₂{N(CN)₂}·4H₂O (**4**), respectively, by IR spectroscopy (**3**) and crystallography (**4**).

[Co{(2-py)₂C(OH)O}₂]₂{N(CN)₂}·4H₂O (4): A solution of Co(O₂CMe)₂·4H₂O (0.112 g, 0.45 mmol) in H₂O (30 mL) was slowly added to a stirred solution of (2-py)₂CO (0.184 g, 1.00 mmol) in a mixture of MeOH and H₂O (30 mL, 1:3 v/v). The pink solution obtained was stirred while an aqueous solution (5 mL) of Na[N(CN)₂] (0.049 g, 0.50 mmol) was added. The resultant pink solution was stirred overnight under reflux and during this time a noticeable colour change to orange occurred. Slow concentration of this solution at room temperature gave orange crystals suitable for crystallography. When precipitation was judged to be complete, the crystals were collected by filtration, washed with cold MeOH

Table 7. Crystal data and structure refinements for [Mn₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄}]·2(2-py)₂CO·4H₂O (**1**), [Ni₄(O₂CMe)₂{N(CN)₂}₂{(2-py)₂C(OH)O}₄}]·10H₂O (**2**) and [Co{(2-py)₂C(OH)O}₂]₂{N(CN)₂}·4H₂O (**4**).

	1	2	4
Empirical formula	C ₇₄ H ₆₆ Mn ₄ N ₁₈ O ₁₈	C ₅₂ H ₆₂ Ni ₄ N ₁₄ O ₂₂	C ₂₄ H ₂₆ CoN ₇ O ₈
Mol. mass	1715.21	1470.00	599.45
Colour and habit	yellow prisms	green prisms	reddish-pink prisms
Crystal size [mm]	0.15 × 0.30 × 0.50	0.10 × 0.25 × 0.45	0.15 × 0.16 × 0.18
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	18.00(1)	13.316(8)	8.148(4)
<i>b</i> [Å]	15.409(9)	19.31(1)	8.866(3)
<i>c</i> [Å]	14.913(9)	13.186(7)	10.316(3)
α [°]	86.26(2)	96.17(2)	70.23(2)
β [°]	66.89(2)	111.65(2)	71.84(3)
γ [°]	85.93(2)	98.35(2)	76.20(3)
<i>V</i> [Å ³]	3791(4)	3070(3)	658.9(4)
<i>Z</i>	2	2	1
$\rho_{\text{calcd.}}$ [Mg m ⁻³]	1.503	1.590	1.511
<i>T</i> [°C]	25	25	20
λ (Mo- <i>K</i> _α) [Å]	0.71073	0.71073	0.71069
μ [mm ⁻¹]	0.734	1.297	0.713
<i>F</i> (000)	1760	1520	306
2 θ_{max} [°]	47.0	47.5	53.0
Index ranges	−20 ≤ <i>h</i> ≤ 18 −17 ≤ <i>k</i> ≤ 17 −16 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 15 −21 ≤ <i>k</i> ≤ 21 −14 ≤ <i>l</i> ≤ 13	−9 ≤ <i>h</i> ≤ 9 −11 ≤ <i>k</i> ≤ 10 −12 ≤ <i>l</i> ≤ 12
No. of reflections collected	11718	9816	2978
No. of indep. refls./ <i>R</i> _{int}	11213/0.0414	9330/0.0280	2645/0.033
Data with <i>I</i> > 2 σ (<i>I</i>)	9082	7009	2465
Parameters refined	1239	977	191
[Δ/σ] _{max}	0.001	0.068	0.005
GOF (on <i>F</i> ²)	1.123	1.083	1.051
<i>R</i> ₁ ^[a]	0.0492	0.0463	0.0383
<i>wR</i> ₂ ^[b]	0.1246	0.1130	0.1046
Residuals [e Å ⁻³]	0.938/−0.422	0.756/−0.420	0.48/−0.56

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = \{\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

(1 mL), Et₂O (2 × 3 mL) and dried in air. Yields (based on Co) as high as 0.19 g (≈ 70%) were obtained. C₂₄H₂₆CoN₇O₈ (599.46): calcd. C 48.1, H 4.4, N 16.4; found C 47.4, H 4.2, N 16.2. IR data (KBr pellet): $\tilde{\nu}$ = 3500 (s, broad), 3442 (m, broad), 3120 (w), 2821 (w), 2275 (m), 2238 (s), 2191 (m), 1642 (sh), 1610 (m), 1470 (sh), 1454 (m), 1390 (w), 1343 (w), 1312 (s), 1249 (s), 1233 (m), 1170 (m), 1029 (s), 950 (w), 903 (w), 824 (m), 762 (s), 699 (m), 683 (m), 573 (m), 525 (w), 494 (w), 479 (w), 455 (w) cm⁻¹.

X-ray Crystallographic Studies: Crystals of **1** and **2** were mounted in capillaries filled with drops of mother liquor while a crystal of **4** was mounted on a glass fibre. Diffraction measurements for **1** and **2** were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo-K α radiation. Data for **4** were collected on a modified STOE 4-circle diffractometer also with graphite-monochromated Mo-K α radiation. Complete crystal data and parameters for data collection and refinements are listed in Table 7. Unit-cell dimensions were determined and refined using the angular settings of 25 (for **1** and **2**) or 36 (for **4**) automatically centred reflections in the ranges $11 < 2\theta < 23^\circ$ (for **1** and **2**) or $10 < 2\theta < 15^\circ$ (for **4**). Three standard reflections monitored every 97 (for **1** and **2**) or 100 (for **4**) reflections showed less than 3% variation and no decay. For **1** and **2**, Lorentz, polarisation and Ψ -scan absorption corrections were applied using the Crystal Logic software package whereas for **4** the data were processed without an absorption correction. The structures were solved by direct methods using SHELXS-86^[43a] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93^[43b] or using the SHELXTL/PC program package^[43c] (for **4**). For all three structures the ordered non-hydrogen atoms were refined anisotropically. In the case of **4**, disordered lattice water molecules containing O(4) and O(5) were refined anisotropically with split occupancies of 0.60(2) and 0.40(2), respectively. Further isotropic displacement parameters, split occupancies of 0.50 and geometrical constraints were applied to N(11), C(12), N(13), C(14) and N(15) of the disordered dicyanamide anion. For **1** and **2**, all hydrogen atoms [except those of the acetate ligands which were introduced in calculated positions as riding on their parent carbon atoms] were located from difference maps and refined isotropically. No hydrogen atoms of the solvate molecules were introduced in the refinements. In the case of **4**, hydrogen atoms of water molecules were fixed in positions located from difference maps. The remaining hydrogen atoms were introduced in calculated positions as riding on their parent atoms. Unit-cell determination (at 25 °C) proved that complex **3** is isostructural with **2**. The unit-cell dimensions of **3** are: $a = 13.54$, $b = 19.13$, $c = 13.16$ Å, $\alpha = 95.21$, $\beta = 111.09$, $\gamma = 98.07^\circ$, $V = 3110$ Å³.

CCDC-246277 (for **1**), 246278 (for **2**) and 246279 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

A. E. and R. V. wish to thank the Spanish Ministerio de Ciencia y Tecnología (BQU2003/0538 project) and G. S. P. and S. P. P. wish to thank the Research Committee of the University of Patras (K. CARATHEODORY Program No 1941) for financial support of this work. F. A. M. thanks Profs. C. Kratky and F. Belaj (Univ. Graz) for use of equipment.

[1] For reviews, see a) R. E. P. Winpenny, *Adv. Inorg. Chem.* **2001**, 52, 1–111; b) R. E. P. Winpenny, *Dalton Trans.* **2002**, 1–10.

- [2] a) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, 43, 2117–2121; b) M. Murugesu, K. A. Abboud, G. Christou, *Dalton Trans.* **2003**, 4552–4556; c) S. Langley, M. Helliwell, J. Raftery, E. I. Tolis, R. E. P. Winpenny, *Chem. Commun.* **2004**, 142–143; d) L. F. Jones, E. K. Brechin, D. Collison, A. Harrison, S. J. Teat, W. Wernsdorfer, *Chem. Commun.* **2002**, 2974–2975; e) T. K. Paine, E. Rentschler, T. Weyhermüller, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2003**, 3167–3178; f) J. Overgaard, B. B. Iversen, S. P. Pali, G. A. Timco, N. V. Gerbeleu, F. K. Larsen, *Chem. Eur. J.* **2002**, 8, 2775–2786; g) X. Liu, J. A. McAllister, M. P. de Miranda, E. J. L. McInnes, C. A. Kilner, M. A. Halcrow, *Chem. Eur. J.* **2004**, 10, 1827–1837; h) T. S. M. Abedin, L. K. Thompson, D. O. Miller, E. Krupicka, *Chem. Commun.* **2003**, 708–709; i) M. Murugesu, C. E. Anson, A. K. Powell, *Chem. Commun.* **2002**, 1054–1055; j) G. L. Abati, A. Cornia, A. C. Fabretti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1998**, 37, 1430–1431.
- [3] For excellent reviews see: a) D. Gatteschi, R. Sessoli, *Angew. Chem. Int. Ed.* **2003**, 42, 268–297; b) G. Christou, D. Gatteschi, D. N. Hendrickson, *MRS Bull.* **2000**, 25, 66–71.
- [4] a) J. R. Friedman, M. P. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, 76, 3830–3833; b) L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, 383, 145–147; c) W. Wernsdorfer, R. Sessoli, *Science* **1999**, 284, 133–135.
- [5] M. N. Leuenberger, D. Loss, *Nature* **2001**, 410, 789–793.
- [6] a) H. J. Eppley, H. L.-Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, 117, 301–317; b) M. Soler, S. K. Chandra, D. Ruiz, E. R. Davidson, D. N. Hendrickson, G. Christou, *Chem. Commun.* **2000**, 2417–2418.
- [7] For recent examples, see: a) C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2003**, 42, 3763–3766; b) C. P. Berlinguette, D. Vaughn, C. Canãda-Vilalta, J. R. Galán-Mascarós, K. R. Dunbar, *Angew. Chem. Int. Ed.* **2003**, 42, 1523–1526; c) H. Zhao, C. P. Berlinguette, J. Bacsá, A. V. Prosvirin, J. K. Bera, S. E. Tichy, E. J. Schelter, K. R. Dunbar, *Inorg. Chem.* **2004**, 43, 1359–1369; d) L. M. Wittick, K. S. Murray, B. Moubarak, S. R. Batten, L. Spiccia, K. J. Berry, *Dalton Trans.* **2004**, 1003–1011; e) C. J. Milios, C. P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S. P. Perlepes, A. Escuer, *Angew. Chem. Int. Ed.* **2004**, 43, 210–212; f) E. C. Sanudo, W. Wernsdorfer, K. A. Abboud, G. Christou, *Inorg. Chem.* **2004**, 43, 4137–4144, and references cited therein. g) M. Soler, W. Wernsdorfer, K. Folting, M. Pink, G. Christou, *J. Am. Chem. Soc.* **2004**, 126, 2156–2165; h) V. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, 126, 4666–4767; i) N. E. Chakov, W. Wernsdorfer, K. A. Abboud, D. N. Hendrickson, G. Christou, *Dalton Trans.* **2003**, 2243–2248; j) S. Hill, R. S. Edwards, N. Aliaga-Alcalde, G. Christou, *Science* **2003**, 302, 1015–1018; k) M. Soler, W. Wernsdorfer, Z. Sun, J. C. Huffman, D. N. Hendrickson, G. Christou, *Chem. Commun.* **2003**, 2672–2673; l) E. K. Brechin, M. Soler, G. Christou, M. Helliwell, S. J. Teat, W. Wernsdorfer, *Chem. Commun.* **2003**, 1276–1277; m) H. Miyasaka, R. Clérac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K. Sugiyama, M. Yamashita, *Angew. Chem. Int. Ed.* **2004**, 43, 2801–2805.
- [8] S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1998**, 120, 2365–2375.
- [9] a) H. Oshio, N. Hoshino, T. Ito, *J. Am. Chem. Soc.* **2000**, 122, 12602–12603; b) A. K. Boudalis, B. Donnadiou, V. Nastopoulos, J. M. Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues, S. P. Perlepes, *Angew. Chem. Int. Ed.* **2004**, 43, 2266–2270.
- [10] a) A. L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, 121, 5302–5310; b) A. Bouwen, A. Caneschi, D. Gatteschi, E. Goovaerts, D. Schoemaker, L. Sorace, M. Stefan, *J. Phys. Chem. B* **2001**, 105, 2658–2663; c) R. W. Saalfrank, I.

- Bernt, M. M. Chowdry, F. Hampel, G. B. M. Vaughan, *Chem. Eur. J.* **2001**, *7*, 2765–2769; d) A. Cornia, A. C. Fabretti, P. Garrisi, C. Mortaló, D. Bonacchi, D. Gatteschi, R. Sessoli, L. Sorace, W. Wernsdorfer, A.-L. Barra, *Angew. Chem. Int. Ed.* **2004**, *43*, 1136–1139; e) C. Benelli, J. Cano, Y. Journaux, R. Sessoli, G. A. Solan, R. E. P. Winpenny, *Inorg. Chem.* **2001**, *40*, 188–189; f) J. C. Goodwin, R. Sessoli, D. Gatteschi, W. Wernsdorfer, A. K. Powell, S. L. Heath, *J. Chem. Soc., Dalton Trans.* **2000**, 1835–1840.
- [11] a) M. Murrie, S. J. Teat, H. Stoeckli-Evans, H. U. Güdel, *Angew. Chem. Int. Ed.* **2003**, *42*, 4653–4656; b) E.-C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezma-Gairaud, G. Christou, *J. Appl. Phys.* **2002**, *91*, 7382–7384.
- [12] a) H. Andres, R. Basler, A. J. Blake, C. Cadiou, G. Chaboussant, C. M. Grant, H.-U. Güdel, M. Murrie, S. Parsons, C. Paulsen, F. Semadini, V. Villar, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Eur. J.* **2002**, *8*, 4867–4876; b) E.-C. Yang, W. Wernsdorfer, S. Hill, R. S. Edwards, M. Nakano, S. Maccagnano, L. N. Zakharov, A. L. Rheingold, G. Christou, D. N. Hendrickson, *Polyhedron* **2003**, *22*, 1727–1733; c) S. T. Ochsenbein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, C. Sekime, H. U. Güdel, *Inorg. Chem.* **2002**, *41*, 5133–5140; d) M. Moragues-Cánovas, M. Helliwell, L. Ricard, E. Rivière, W. Wernsdorfer, E. Brechin, T. Mallah, *Eur. J. Inorg. Chem.* **2004**, 2219–2222.
- [13] J. J. Sokol, A. G. Hee, J. R. Long, *J. Am. Chem. Soc.* **2002**, *124*, 7656–7657.
- [14] For a review, see: G. S. Papaefstathiou, S. P. Perlepes, *Comments Inorg. Chem.* **2002**, *23*, 249–274.
- [15] a) C. J. Milios, E. Kefalloniti, C. P. Raptopoulou, A. Terzis, R. Vicente, N. Lalioti, A. Escuer, S. P. Perlepes, *Chem. Commun.* **2003**, 819–821; b) N. Lalioti, C. P. Raptopoulou, A. Terzis, A. E. Aliev, I. P. Gerothanassis, E. Manessi-Zoupa, S. P. Perlepes, *Angew. Chem. Int. Ed.* **2001**, *40*, 3211–3214; c) A. Tsohos, S. Dionysopoulou, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassiss, S. P. Perlepes, *Angew. Chem. Int. Ed.* **1999**, *38*, 983–985; d) V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, E. G. Bakalbassiss, S. P. Perlepes, A. Terzis, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1083–1085; e) V. Tangoulis, C. P. Raptopoulou, A. Terzis, S. Paschalidou, S. P. Perlepes, E. G. Bakalbassiss, *Inorg. Chem.* **1997**, *36*, 3996–4006.
- [16] a) M.-L. Long, S.-L. Zheng, J.-X. Shi, Y.-X. Tong, H. K. Lee, X.-M. Chen, *Dalton Trans.* **2002**, 1727–1734; b) S. B. Jedner, H. Schwöppe, H. Nimir, A. Rempel, D. A. Brown, B. Krebs, *Inorg. Chim. Acta* **2002**, *340*, 181–186; c) S. R. Breeze, S. Wang, J. E. Greedan, N. P. Raju, *Inorg. Chem.* **1996**, *35*, 6944–6951.
- [17] Representative literature: a) K. N. Crowder, S. J. Garcia, R. L. Burr, J. M. North, M. H. Wilson, B. L. Conley, P. E. Fanwick, P. S. White, K. D. Siennerth, R. M. Granger II, *Inorg. Chem.* **2004**, *43*, 72–78; b) G. Crundwell, B. L. Westcott, R. Coffey, M. Zeller, A. D. Hunter, *Inorg. Chim. Acta* **2003**, *355*, 432–437; c) J. Woltz, B. L. Westcott, G. Crundwell, M. Zeller, A. D. Hunter, S. O. Sommerer, *Acta Crystallogr., Sect. E* **2002**, *58*, 609–610; d) A. K. Boudalis, F. Dahan, A. Bousseksou, J.-P. Tuchagues, S. P. Perlepes, *Dalton Trans.* **2003**, 3411–3418; e) E. Katsoulakou, N. Lalioti, C. P. Raptopoulou, A. Terzis, E. Manessi-Zoupa, S. P. Perlepes, *Inorg. Chem. Commun.* **2002**, *5*, 719–723; f) S. Zhou, W. W. Brennessel, R. G. Harrison, L. Que, Jr., *Inorg. Chim. Acta* **2002**, *337*, 32–38; g) M. G. Barandika, Z. Serna, R. Cortes, L. Lezama, M. K. Urriaga, M. I. Arriortua, T. Rojo, *Chem. Commun.* **2001**, 45–46; h) Z. E. Serna, R. Cortes, M. K. Urriaga, M. G. Barandika, L. Lezama, M. I. Arriortua, T. Rojo, *Eur. J. Inorg. Chem.* **2001**, 865–872; i) M.-L. Tong, H. K. Lee, Y.-X. Tong, X.-M. Chen, T. C. W. Mak, *Inorg. Chem.* **2000**, *39*, 4666–4669; j) V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, A. Tsohos, E. G. Bakalbassiss, A. Terzis, S. P. Perlepes, *Inorg. Chem.* **1997**, *36*, 5270–5277; k) A. C. Deveson, S. L. Heath, C. J. Harding, A. K. Powell, *J. Chem. Soc., Dalton Trans.* **1996**, 3173–3178; l) A. N. Papadopoulos, V. Tangoulis, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **1996**, *35*, 559–565.
- [18] a) G. S. Papaefstathiou, A. Escuer, M. Font-Bardia, S. P. Perlepes, X. Solans, R. Vicente, *Polyhedron* **2002**, *21*, 2027; b) G. S. Papaefstathiou, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, S. P. Perlepes, *Chem. Commun.* **2001**, 2414–2415; c) G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, *Angew. Chem. Int. Ed.* **2001**, *40*, 884–886.
- [19] a) Z. E. Serna, L. Lezama, M. K. Urriaga, M. I. Arriortua, M. G. Barandika, R. Cortes, T. Rojo, *Angew. Chem. Int. Ed.* **2000**, *39*, 344–347; b) Z. E. Serna, M. G. Barandika, R. Cortes, M. K. Urriaga, G. E. Barberis, T. Rojo, *J. Chem. Soc., Dalton Trans.* **2000**, 29–34; c) Z. E. Serna, M. K. Urriaga, M. G. Barandika, R. Cortes, S. Martin, L. Lezama, M. I. Arriortua, T. Rojo, *Inorg. Chem.* **2001**, *40*, 4550–4555; d) G. S. Papaefstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, R. Vicente, *Eur. J. Inorg. Chem.* **2001**, 1567–1574.
- [20] S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* **2003**, *246*, 103–130.
- [21] A. M. Kutasi, A. R. Harris, S. R. Batten, B. Moubaraki, K. S. Murray, *Cryst. Growth Des.* **2004**, *4*, 605–610, and references therein.
- [22] Representative literature: a) B. Vangdal, J. Carranza, F. Lloret, M. Julve, J. Sletten, *Dalton Trans.* **2002**, 566–574, and references cited therein. b) A. M. Kutasi, S. R. Batten, B. Moubaraki, K. S. Murray, *Dalton Trans.* **2002**, 819–821; c) A. Escuer, F. A. Mautner, N. Sanz, R. Vicente, *Inorg. Chim. Acta* **2002**, *340*, 163–169; d) A. Escuer, F. A. Mautner, N. Sanz, R. Vicente, *Inorg. Chem.* **2000**, *39*, 1668–1673; e) J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold, J. S. Miller, *J. Solid State Chem.* **1999**, *145*, 369–378; f) J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein, J. S. Miller, *Chem. Mater.* **1998**, *10*, 2552–2560; g) M. Kurmoo, C. J. Kepert, *New J. Chem.* **1998**, *22*, 1515–1524; h) J. L. Manson, J. A. Schlueter, H.-J. Koo, M.-H. Whangbo, *Inorg. Chem.* **2004**, *43*, 4007–4011; i) B. Jürgens, H. A. Höpfe, W. Schnick, *Solid State Sci.* **2002**, *4*, 821–825.
- [23] M.-L. Tong, Y.-M. Wu, Y.-X. Tong, X.-M. Chen, H.-C. Chang, S. Kitagawa, *Eur. J. Inorg. Chem.* **2003**, 2385–2388.
- [24] J. M. Seco, M. Quiros, M. J. González Garmendia, *Polyhedron* **2000**, *19*, 1005–1013.
- [25] R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* **2000**, 2349–2356.
- [26] J. M. Clemente-Juan, B. Chansou, B. Donnadieu, J.-P. Tuchagues, *Inorg. Chem.* **2000**, *39*, 5515–5519.
- [27] a) C. J. Milios, E. Kefalloniti, C. P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S. P. Perlepes, *Polyhedron* **2004**, *23*, 83–95; b) C. J. Milios, T. C. Stamatatos, P. Kyritsis, A. Terzis, C. P. Raptopoulou, R. Vicente, A. Escuer, S. P. Perlepes, *Eur. J. Inorg. Chem.* **2004**, 2885–2901.
- [28] a) L. E. Pence, A. Caneschi, S. J. Lippard, *Inorg. Chem.* **1996**, *35*, 3069–3072; b) S. Brooker, V. McKee, T. Metcalfe, *Inorg. Chim. Acta* **1996**, *246*, 171–79; c) P. Guerriero, S. Tamburini, P. A. Vigato, *Coord. Chem. Rev.* **1995**, *139*, 17–243; d) K. L. Taft, A. Caneschi, L. E. Pence, C. D. Delfs, G. C. Papaefthymiou, S. Lippard, *J. Am. Chem. Soc.* **1993**, *115*, 11753–11766; e) S. Brooker, V. McKee, W. B. Shepard, L. K. Pannell, *J. Chem. Soc., Dalton Trans.* **1987**, 255–2562.
- [29] K. S. Murray, *Adv. Inorg. Chem.* **1995**, *43*, 261–358.
- [30] a) J. E. Andrew, A. B. Blake, *J. Chem. Soc. A* **1969**, 1556–1560; b) V. G. Kessler, S. Golih, M. Kritikos, O. N. Korsak, E. E. Knyazeva, I. F. Moskovskaya, B. V. Romanovsky, *Polyhedron* **2001**, *20*, 915–922; c) M. A. Halcrow, J.-S. Sun, J. C. Huffman, G. Christou, *Inorg. Chem.* **1995**, *34*, 4167–4177; d) M. S. El Fallah, E. Rentschler, A. Caneschi, D. Gatteschi, *Inorg. Chim. Acta* **1996**, *247*, 231–235; e) A. J. Blake, E. K. Brechin, A. Gordon, R. O. Gould, C. M. Grant, S. Parsons, J. M. Rawson,

- R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.* **1995**, 1983–1984.
- [31] a) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2003**, 863–875; b) G. Aromi, A. S. Batsanov, P. Christian, M. Helliwell, O. Roubeau, G. A. Timco, R. E. P. Winpenny, *Dalton Trans.* **2003**, 4466–4471; c) A. K. Sah, C. P. Rao, P. K. Sarenketo, K. Rissanen, *Chem. Lett.* **2001**, 1296–1297; d) A. Escuer, M. Font-Bardia, S. B. Kumar, X. Solans, R. Vicente, *Polyhedron* **1999**, *18*, 909–914; e) W. Vreugdenhil, J. G. Haasnoot, J. Reedijk, A. L. Spek, *Inorg. Chim. Acta* **1987**, *129*, 205–216, and references therein.
- [32] a) G. Aromi, A. S. Batsanov, P. Christian, M. Helliwell, A. Par-kin, S. Parsons, A. A. Smith, G. A. Timco, R. E. P. Winpenny, *Chem. Eur. J.* **2003**, *9*, 5142–5161; b) K. E. Gubina, V. A. Ovchinnikov, J. Swiatek-Kozłowska, V. M. Amirkhanov, T. Yu. Silva, K. V. Domasevitch, *Polyhedron* **2002**, *21*, 963–967; c) M. M. Olmstead, P. P. Power, G. A. Sigel, *Inorg. Chem.* **1988**, *27*, 580–583; d) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, R. C. Sherwood, *Inorg. Chem.* **1971**, *10*, 240–246.
- [33] R. H. Holm, S. Ciurli, J. A. Weigel, *Prog. Inorg. Chem.* **1990**, *38*, 1–74.
- [34] G. W. Brudvig, H. H. Thorp, R. H. Crabtree, *Acc. Chem. Res.* **1991**, *24*, 311–316.
- [35] For example, see: a) K. Wieghardt, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1153–1172; b) M. W. Wemple, H.-L. Tsai, K. Folting, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1993**, *32*, 2025, and references cited therein. c) A. Rompel, J. C. Andrews, R. M. Cinco, M. W. Wemple, G. Christou, N. A. Law, V. L. Pecoraro, K. Sauer, V. K. Yachandra, M. P. Lein, *J. Am. Chem. Soc.* **1997**, *119*, 4465–4470.
- [36] K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber, S. Iwata, *Science* **2004**, *303*, 1831–1838.
- [37] J. A. Bertrand, C. Marbela, D. G. Vanderneer, *Inorg. Chim. Acta* **1978**, *26*, 113–118.
- [38] a) S. O. Sommerer, J. D. Baker, W. P. Jensen, A. Hamza, R. A. Jacobson, *Inorg. Chim. Acta* **1993**, *210*, 173–176; b) M.-L. Tong, G. Yang, X.-M. Chen, S. W. Ng, *Acta Crystallogr., Sect. C* **1998**, *54*, 217–219; c) C. Hemmert, M. Renz, H. Gornitzka, S. Soulet, B. Meunier, *Chem. Eur. J.* **1999**, *5*, 1766–1774.
- [39] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.
- [40] D. Gatteschi, L. Pardi, *Gazz. Chim. Ital.* **1993**, *123*, 231–238.
- [41] L. Ballester, E. Coronado, A. Gutiérrez, A. Monge, M. F. Perpinan, E. Pinilla, T. Rico, *Inorg. Chem.* **1992**, *31*, 2053–2056.
- [42] J. J. Smit, G. M. Nap, L. J. De Jongh, J. A. C. van Ooijen, J. Reedijk, *Physica B* **1979**, *97*, 365–371.
- [43] a) G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1986**; b) G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**; c) G. M. Sheldrick, *SHELXTL/PC*, Release 5.03, Siemens Analytical X-ray Instruments, Madison, WI, **1994**.

Received: August 2, 2004