

# Use of the Sulfato Ligand in 3d-Metal Cluster Chemistry: A Family of Hexanuclear Nickel(II) Complexes with 2-Pyridyl-Substituted Oxime Ligands

Constantina Papatriantafyllopoulou,<sup>[a]</sup> Guillem Aromi,<sup>[b]</sup> Anastasios J. Tasiopoulos,<sup>[c]</sup> Vassilios Nastopoulos,<sup>[a]</sup> Catherine P. Raptopoulou,<sup>[d]</sup> Simon J. Teat,<sup>\*,[e]</sup> Albert Escuer,<sup>\*,[b]</sup> and Spyros P. Perlepes<sup>\*,[a]</sup>

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The initial use of 2-pyridyl-substituted oximes [(py)C(R)-NOH; R = Me, Ph]/sulfate blend in nickel(II) chemistry has yielded a family of hexanuclear clusters. The syntheses, structures and magnetic properties are reported of [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>-(OH){(py)C(Me)NO}<sub>3</sub>{(py)C(Me)NOH}<sub>3</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)} (**1**), [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(Ph)NO}<sub>3</sub>{(py)C(Ph)NOH}<sub>3</sub>(MeOH)<sub>3</sub>] (**2**) and [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(Ph)NO}<sub>3</sub>{(py)C(Ph)NOH}<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] (**3**), where (py)C(Me)NOH is methyl 2-pyridyl ketone oxime and (py)C(Ph)NOH is phenyl 2-pyridyl ketone oxime. The hexanuclear molecules present in the three complexes have similar structures which contain the [Ni<sub>6</sub>(μ<sub>3</sub>-OH)(μ<sub>3</sub>-SO<sub>4</sub>)<sub>3</sub>(μ<sub>3</sub>-ONR)<sub>3</sub>]<sup>2+</sup> core. The core consists of six Ni<sup>II</sup> ions arranged as

two parallel equilateral triangular subunits, one small (Ni...Ni ca. 3.3 Å) and the other larger (Ni...Ni ca. 6.0 Å). Characteristic IR bands are discussed in terms of the known structures of **1–3**. The magnetic properties of **1** and **2** have been studied by variable-temperature dc magnetic susceptibility techniques which indicate antiferromagnetic interactions. A simple 2-*J* model was found to be adequate to describe the similar thermal variation of the molar magnetic susceptibilities of **1** and **2**.

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## Introduction

There continues to be a great interest in the synthesis and physicochemical study of polynuclear metal complexes (clusters) containing paramagnetic metal ions. Among the reasons for this is the search for various nuclearity oxido-bridged metal clusters to model M<sub>x</sub> sites in biomolecules.<sup>[1]</sup> In addition, 3d-metal clusters often display interesting and sometimes novel magnetic properties, including high ground state spin values, currently up to *S* = 83/2,<sup>[2]</sup> and single-molecule magnetism (SMM) behavior.<sup>[3]</sup> Crucial to such efforts and others is the continuing development of new synthetic procedures to polynuclear species. However, there is no obvious and guaranteed route to such species.<sup>[4]</sup> The lack of control has led to the neologism “self-assembly” being introduced.

In recent years several groups have been introducing an element of design into the assembly process by choosing rigid ligands with predictable and controllable binding modes.<sup>[5–7]</sup> Other researchers use a complementary approach named “serendipitous assembly”,<sup>[8]</sup> where the variables in the reaction system are modified following certain rationales to influence the product found, rather than to control or design the target molecule. Since it is clear that inorganic chemists cannot simply trust to luck in preparing metal clusters, there has to be considerable forethought in the ligands, metals and conditions used for any significant progress to be made.<sup>[9]</sup>

With the points mentioned above in mind, and in the context of “serendipitous assembly”,<sup>[8]</sup> our group<sup>[10]</sup> and others<sup>[11]</sup> have been exploring “ligand blend” reactions involving the monoanions (py)C(R)NO<sup>−</sup> of various 2-pyridyl-substituted oximes<sup>[12]</sup> [Figure 1; R can be a non-donor group or a group containing an extra donor site, i.e. a second 2-pyridyl group in the particular case of di-2-pyridyl ketone oximate (py)<sub>2</sub>CNO<sup>−</sup> and carboxylates, *with* or *without* additional inorganic monoanions (Cl<sup>−</sup>, Br<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, N<sub>3</sub><sup>−</sup>, SCN<sup>−</sup>), with the belief that they might foster formation of transition-metal clusters. The immense structural diversity displayed by the complexes reported stems in part from the ability of (py)C(R)NO<sup>−</sup> to exhibit many distinct bridging coordination modes. Employment of additional inorganic monoanions with a good coordination capacity gives an ex-

[a] Department of Chemistry, University of Patras, 26504 Patras, Greece  
E-mail: perlepes@patreas.upatras.gr

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

[c] Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

[d] Institute of Materials Science, NCSR “Demokritos”, 15310 Aghia Paraskevi Attikis, Greece

[e] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Mail stop 2-400, Berkeley, CA 94720, USA  
E-mail: SJTeat@lbl.gov

traordinary structural versatility in the *ternary* ligand systems. Thus, the (py)C(R)NO<sup>−</sup>/R'CO<sub>2</sub><sup>−</sup> (R = H, Me, Ph, py; R' = H, Me, Et, Ph) “blends”, without or with additional inorganic anions (Cl<sup>−</sup>, Br<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, N<sub>3</sub><sup>−</sup>, SCN<sup>−</sup>) have led to a variety of Cr, Mn, Fe, Co, Ni and Cu clusters<sup>[10–12]</sup> with nuclearities ranging from 3 to 12 and with interesting magnetic properties, including SMM behavior.<sup>[10h,10n]</sup>

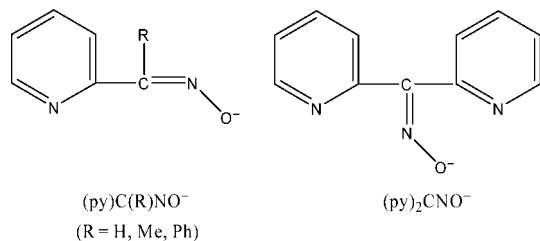


Figure 1. The structural formulae and abbreviations of the ligands discussed in the text.

Very recently we decided to begin a program which can be considered as a modification of the above *binary* ligand system approach. We have been exploring the use of the sulfato ligand, SO<sub>4</sub><sup>2−</sup>, instead of the carboxylato ligand, R'CO<sub>2</sub><sup>−</sup>. The great coordinative flexibility and versatility of the (py)C(R)NO<sup>−</sup> ligands, as well as the μ<sub>2</sub>, μ<sub>3</sub>, μ<sub>4</sub>, μ<sub>5</sub> or μ<sub>6</sub> potential of SO<sub>4</sub><sup>2−</sup> (Figure 2),<sup>[13]</sup> prompted as to combine the 2-pyridyl oximates with the sulfate ligand to aim for

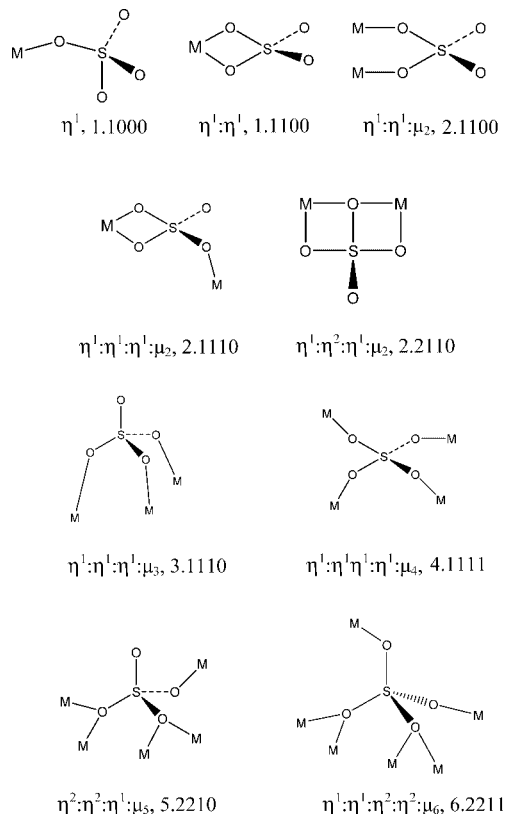


Figure 2. The up to now crystallographically established coordination modes of the sulfato ligand, and the η/μ and Harris<sup>[21]</sup> notations which describe these modes. The novel η<sup>1</sup>:η¹:μ<sub>3</sub> (3.2100) ligation mode that appears in the clusters described here is not included (see Figure 4).

new types of clusters. Our belief was that the simultaneous employment of the two ligand types in 3d-metal chemistry would give structural flexibility in the (py)C(R)NO<sup>−</sup>/SO<sub>4</sub><sup>2−</sup> “blends”. The possible advantages of using SO<sub>4</sub><sup>2−</sup> instead of R'CO<sub>2</sub><sup>−</sup> include (i) the possibility of triggering aggregation of preformed smaller cationic species<sup>[14]</sup> containing *only* (py)C(R)NO<sup>−</sup> into new, higher-nuclearity products, and (ii) the possible diversion of known reaction systems developed using *monoanionic* carboxylates to new species as a result of the higher charge and higher denticity/bridging capability of sulfates.

The sulfate ion is currently a ligand of intense interest.<sup>[13,15]</sup> Somewhat to our surprise, the sulfato ligand has not been used in transition-metal cluster chemistry. On the other hand, there is currently a renewed interest in the coordination chemistry of oximes.<sup>[16]</sup> 2-Pyridyl-substituted oximes are a subclass of oxime ligands, currently very popular in several aspects of coordination chemistry.<sup>[12,16c,17]</sup>

We herein report the first use of SO<sub>4</sub><sup>2−</sup> in 3d-metal/2-pyridyloximate chemistry. We describe synthetic procedures to a family of novel hexanuclear Ni<sup>II</sup>/SO<sub>4</sub><sup>2−</sup>/(py)C(R)NO<sup>−</sup> (R = Me, Ph) complexes, which have been characterized by single-crystal X-ray crystallography and IR spectroscopy; the magnetic properties of two representative complexes are also described and analyzed. With one exception,<sup>[18]</sup> the prepared compounds are the first Ni<sup>II</sup>/SO<sub>4</sub><sup>2−</sup> clusters that appear in the literature. Moreover, they allow the initial assessment of ligation tendencies of the SO<sub>4</sub><sup>2−</sup> ion in the coordination chemistry of 2-pyridyl-substituted oximes.

## Results and Discussion

### Synthesis and IR Characterization

The original aim of this synthetic program was to explore the versatile bridging potential of the binary (py)C(R)NO<sup>−</sup>/SO<sub>4</sub><sup>2−</sup> system for the assembly of Ni<sup>II</sup> ions into clusters with novel structures and magnetic properties. Our general synthetic approach for the isolation of heteroleptic Ni<sup>II</sup> clusters was to treat an excess of the metal sulfate with (py)C(R)NOH (R = Me, Ph) and a base in MeOH. The addition of base is necessary for the deprotonation of the organic ligand. Note that reactions in the absence of base lead to complexes [Ni(SO<sub>4</sub>)<sub>2</sub>[(py)C(Me)NOH]<sub>2</sub>(H<sub>2</sub>O)]<sub>3</sub>, [Ni(SO<sub>4</sub>)<sub>2</sub>[(py)C(Me)NOH]<sub>2</sub>(H<sub>2</sub>O)]<sub>2</sub>, [Ni<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>[(py)C(ph)NOH]<sub>4</sub>] and [Ni{(py)C(ph)NOH}<sub>3</sub>](SO<sub>4</sub>)<sup>[19]</sup> that contain the neutral ligands.

Treatment of NiSO<sub>4</sub>·6H<sub>2</sub>O with one equivalent of (py)C(Me)NOH and one equivalent of NaOMe in MeOH gave a green solution from which the hexanuclear cluster [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(Me)NO}<sub>3</sub>{(py)C(Me)NOH}<sub>3</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)] (**1**) was obtained in 65% yield. The methoxide ions act as proton acceptors to facilitate formation of OH<sup>−</sup> and (py)C(Me)NO<sup>−</sup> ligands. Reactions with small variations in the Ni<sup>II</sup>/(py)C(Me)NOH ratio gave the same Ni<sub>6</sub> compound **1**. As expected, the nature of the base is not crucial for the identity of the product; we were able to isolate

**1** by using a plethora of bases such as  $\text{NEt}_3$ ,  $\text{NMe}_4\text{OH}$ ,  $\text{NEt}_4\text{OH}$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  etc. (see Method B in the Experimental Section). Because cluster **1** has a  $\text{Ni}^{\text{II}}$ /organic ligand ratio of 1:1, we wondered whether the hexanuclear complex could be prepared by the reaction of  $[\text{Ni}(\text{SO}_4)\{(\text{py})\text{C}(\text{Me})\text{NOH}\}(\text{H}_2\text{O})_3]$  with the appropriate amount of the base. The conversion of the mononuclear to the hexanuclear complex can be accomplished easily by treatment of the former with the stoichiometric amount of  $\text{LiOH}\cdot\text{H}_2\text{O}$  in  $\text{MeOH}$  at 35–40 °C.

We initially came across complexes  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3(\text{MeOH})_3]$  (**2**) and  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3(\text{H}_2\text{O})_3]$  (**3**) when we tried to prepare the  $(\text{py})\text{C}(\text{ph})\text{NO}/(\text{py})\text{C}(\text{ph})\text{NOH}$  analog of complex **1**. The 1:1:1  $\text{NiSO}_4\cdot 6\text{H}_2\text{O}/(\text{py})\text{C}(\text{ph})\text{NOH}/\text{NaOMe}$  reaction mixture in  $\text{MeOH}$  gave an orange solution, which upon layering with  $\text{Et}_2\text{O}$  yielded crystals that were obviously a mixture of two products. Microscopic ex-

amination showed both greenish-yellow prisms and yellow plates to be present in a visual ratio of roughly 1:1. Their not-too-dissimilar solubility prevented chemical separation; however, the differences in color and crystal shape allowed easy manual separation of the two materials. The prismatic and plate-like crystals were crystallographically identified as complexes **2**·3.2  $\text{MeOH}\cdot 1.5\text{H}_2\text{O}$  and **3**·3  $\text{H}_2\text{O}$ , respectively.

With the identities of **2** and **3** established, convenient syntheses of pure materials were sought under alternative reaction conditions. This was not possible for **2**. Thus, the manual separation of the prismatic crystals from their above-described mixture with **3** remains the only source of complex **2** to date for further measurements. Complex **3** has  $\text{H}_2\text{O}$  molecules as the only solvate ligands; thus attempts to obtain pure **3** were made by adding  $\text{H}_2\text{O}$  in the reaction mixture. Working with an 8:2 (v/v)  $\text{MeOH}/\text{H}_2\text{O}$  solvent mixture, we were lucky enough to isolate the yellow plates of **3** as the only product. It is likely that factors such as

Table 1. Selected interatomic distances [Å] and angles [°] for  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3(\text{MeOH})_2(\text{H}_2\text{O})]\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$  (**1**·2.53  $\text{MeOH}\cdot 1.60\text{H}_2\text{O}$ ).

$\text{Ni}(1)\cdots\text{Ni}(2)$	3.304(4)	$\text{Ni}(3)-\text{N}(6)$	2.047(4)
$\text{Ni}(1)\cdots\text{Ni}(3)$	3.293(4)	$\text{Ni}(4)-\text{O}(1)$	2.058(3)
$\text{Ni}(2)\cdots\text{Ni}(3)$	3.304(4)	$\text{Ni}(4)-\text{O}(12)$	2.028(3)
$\text{Ni}(4)\cdots\text{Ni}(5)$	5.970(4)	$\text{Ni}(4)-\text{O}(17)$	2.078(3)
$\text{Ni}(4)\cdots\text{Ni}(6)$	5.947(4)	$\text{Ni}(4)-\text{OW}(24)$	2.084(3)
$\text{Ni}(5)\cdots\text{Ni}(6)$	6.004(4)	$\text{Ni}(4)-\text{N}(7)$	2.063(4)
$\text{Ni}(1)-\text{O}(2)$	2.061(3)	$\text{Ni}(4)-\text{N}(8)$	2.057(4)
$\text{Ni}(1)-\text{O}(7)$	2.059(3)	$\text{Ni}(5)-\text{O}(3)$	2.057(3)
$\text{Ni}(1)-\text{O}(14)$	2.157(3)	$\text{Ni}(5)-\text{O}(18)$	2.034(3)
$\text{Ni}(1)-\text{O}(23)$	2.008(3)	$\text{Ni}(5)-\text{O}(21)$	2.078(3)
$\text{Ni}(1)-\text{N}(1)$	2.046(4)	$\text{Ni}(5)-\text{OM}(25)$	2.105(4)
$\text{Ni}(1)-\text{N}(2)$	2.045(4)	$\text{Ni}(5)-\text{N}(9)$	2.049(5)
$\text{Ni}(2)-\text{O}(3)$	2.069(3)	$\text{Ni}(5)-\text{N}(10)$	2.056(4)
$\text{Ni}(2)-\text{O}(9)$	2.063(3)	$\text{Ni}(6)-\text{O}(2)$	2.053(3)
$\text{Ni}(2)-\text{O}(21)$	2.128(3)	$\text{Ni}(6)-\text{O}(14)$	2.068(3)
$\text{Ni}(2)-\text{O}(23)$	2.009(4)	$\text{Ni}(6)-\text{O}(22)$	2.033(3)
$\text{Ni}(2)-\text{N}(3)$	2.055(4)	$\text{Ni}(6)-\text{OM}(26)$	2.086(4)
$\text{Ni}(2)-\text{N}(4)$	2.047(4)	$\text{Ni}(6)-\text{N}(11)$	2.060(4)
$\text{Ni}(3)-\text{O}(1)$	2.074(3)	$\text{Ni}(6)-\text{N}(12)$	2.061(4)
$\text{Ni}(3)-\text{O}(8)$	2.060(3)	$\text{S}(3)-\text{O}(15)$	1.464(3)
$\text{Ni}(3)-\text{O}(17)$	2.112(3)	$\text{S}(3)-\text{O}(16)$	1.454(3)
$\text{Ni}(3)-\text{O}(23)$	2.007(3)	$\text{S}(3)-\text{O}(17)$	1.496(3)
$\text{Ni}(3)-\text{N}(5)$	2.056(4)	$\text{S}(3)-\text{O}(18)$	1.463(3)
$\text{O}(2)-\text{Ni}(1)-\text{N}(2)$	175.6(1)	$\text{N}(7)-\text{Ni}(4)-\text{N}(8)$	78.2(2)
$\text{O}(7)-\text{Ni}(1)-\text{O}(14)$	166.5(1)	$\text{O}(3)-\text{Ni}(5)-\text{OM}(25)$	173.0(2)
$\text{O}(14)-\text{Ni}(1)-\text{N}(1)$	90.9(1)	$\text{O}(18)-\text{Ni}(5)-\text{O}(21)$	90.4(1)
$\text{O}(23)-\text{Ni}(1)-\text{N}(1)$	168.4(2)	$\text{O}(18)-\text{Ni}(5)-\text{N}(9)$	168.7(2)
$\text{O}(23)-\text{Ni}(1)-\text{N}(2)$	89.8(2)	$\text{O}(21)-\text{Ni}(5)-\text{N}(10)$	167.9(2)
$\text{O}(3)-\text{Ni}(2)-\text{O}(21)$	77.4(1)	$\text{N}(9)-\text{Ni}(5)-\text{N}(10)$	78.9(2)
$\text{O}(3)-\text{Ni}(2)-\text{N}(4)$	177.4(2)	$\text{O}(2)-\text{Ni}(6)-\text{OM}(26)$	172.7(1)
$\text{O}(9)-\text{Ni}(2)-\text{O}(21)$	165.9(1)	$\text{O}(14)-\text{Ni}(6)-\text{N}(12)$	167.9(2)
$\text{O}(21)-\text{Ni}(2)-\text{N}(4)$	100.4(1)	$\text{O}(22)-\text{Ni}(6)-\text{N}(11)$	170.3(2)
$\text{O}(23)-\text{Ni}(2)-\text{N}(3)$	167.0(2)	$\text{OM}(26)-\text{Ni}(6)-\text{N}(12)$	90.3(2)
$\text{O}(1)-\text{Ni}(3)-\text{N}(6)$	176.5(1)	$\text{N}(11)-\text{Ni}(6)-\text{N}(12)$	77.8(2)
$\text{O}(8)-\text{Ni}(3)-\text{O}(17)$	168.3(1)	$\text{Ni}(1)-\text{O}(23)-\text{Ni}(2)$	110.7(2)
$\text{O}(8)-\text{Ni}(3)-\text{N}(6)$	91.1(1)	$\text{Ni}(1)-\text{O}(23)-\text{Ni}(3)$	110.2(2)
$\text{O}(23)-\text{Ni}(3)-\text{N}(5)$	168.1(2)	$\text{Ni}(1)-\text{O}(2)-\text{Ni}(6)$	103.2(2)
$\text{N}(5)-\text{Ni}(3)-\text{N}(6)$	79.1(2)	$\text{Ni}(1)-\text{O}(14)-\text{Ni}(6)$	99.4(2)
$\text{O}(1)-\text{Ni}(4)-\text{OW}(24)$	173.4(1)	$\text{Ni}(2)-\text{O}(3)-\text{Ni}(5)$	103.0(2)
$\text{O}(12)-\text{Ni}(4)-\text{N}(7)$	167.8(2)	$\text{Ni}(2)-\text{O}(21)-\text{Ni}(5)$	100.3(2)
$\text{O}(17)-\text{Ni}(4)-\text{N}(7)$	91.3(1)	$\text{Ni}(3)-\text{O}(1)-\text{Ni}(4)$	102.3(2)
$\text{O}(17)-\text{Ni}(4)-\text{N}(8)$	168.7(1)	$\text{Ni}(3)-\text{O}(17)-\text{Ni}(4)$	100.4(2)

relatively solubility, lattice energy, crystallization kinetics and nature of the cation of the base, amongst others, determine the identity of the isolated product.

Two features of the reactions deserve comments. First, the reaction mixtures which lead to **1–3** should be filtered before crystallization to remove  $\text{Na}_2\text{SO}_4$  or  $\text{Li}_2\text{SO}_4$  which are insoluble in MeOH; the filtration is not necessary for the preparation of pure **3**. The products also need to be washed with a small amount of  $\text{H}_2\text{O}$  to ensure complete removal of the alkali sulfate. Second, the addition of counter anions such as  $\text{ClO}_4^-$  and  $\text{PF}_6^-$  (for the isolation of potentially existing cationic species) and the crystallization method have no influence on the identity of the products.

The IR spectra of air-dried samples of complexes **1**, **2** and **3** exhibit a shoulder at  $3430\text{--}3400\text{ cm}^{-1}$  and one broad band of medium intensity at  $3410\text{--}3255\text{ cm}^{-1}$  assignable to  $\nu(\text{OH})$  vibrations of  $\text{OH}^-$ ,  $(\text{py})\text{C}(\text{R})\text{NOH}$ ,  $\text{H}_2\text{O}$  and/or MeOH. Complexes **1–3** have  $C_1$  symmetry at their sulfato ligands. The bands at about  $1180\text{--}1150$ ,  $1130$  and  $1030\text{ cm}^{-1}$  are therefore attributed<sup>[20]</sup> to the  $\nu_3$  modes, while the bands

at about  $690$ ,  $630$  and  $590\text{ cm}^{-1}$  are assigned<sup>[20]</sup> to the  $\nu_4$  modes with the higher wavenumber band being superimposed by ligands' vibrations. The band at  $1652$  (**1**) and ca.  $1600$  (**2**, **3**) is assigned to the oximate  $\nu(\text{C}=\text{N})$  vibrational mode;<sup>[9d]</sup> in **2** and **3** this band may also have an aromatic stretch character. The appearance of many bands in the  $1200\text{--}1000\text{ cm}^{-1}$  region and possible overlap with the sulfato stretching vibration renders exact assignments of the two expected<sup>[14c]</sup>  $\nu(\text{N}=\text{O})$  modes difficult; a strong band at  $1070$  (**1**) and ca.  $1050$  (**2**, **3**)  $\text{cm}^{-1}$  is a serious candidate for this vibration.<sup>[14a,14b]</sup>

### Description of Structures

Partially labelled plots of the hexanuclear molecules present in **1**· $2.53\text{ MeOH}\cdot 1.60\text{ H}_2\text{O}$ , **2**· $3.2\text{ MeOH}\cdot 1.5\text{ H}_2\text{O}$  and **3**· $3\text{ H}_2\text{O}$  are shown in Figures 3, 7 and 8, respectively. Selected interatomic distances and angles are listed in Tables 1, 2 and 3. Tables 4, 5 and 6 summarize intracluster hydrogen bonding data for the three complexes. The molecu-

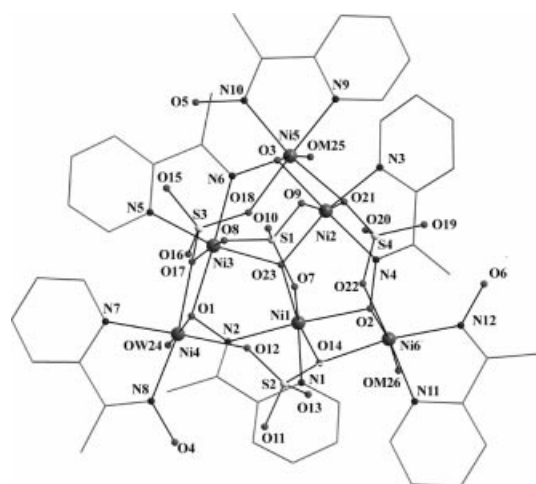
Table 2. Selected interatomic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3(\text{MeOH})_3]\cdot 3.2\text{ MeOH}\cdot 1.5\text{ H}_2\text{O}$  (**2**· $3.2\text{ MeOH}\cdot 1.5\text{ H}_2\text{O}$ ).

Ni(1)···Ni(3)	5.967(9)	Ni(3)–OM(2)	2.088(5)
Ni(1)···Ni(4)	5.994(9)	Ni(3)–N(41)	2.086(6)
Ni(2)···Ni(5)	3.293(9)	Ni(3)–N(42)	2.047(6)
Ni(2)···Ni(6)	3.306(9)	Ni(4)–O(21)	2.064(5)
Ni(3)···Ni(4)	5.977(9)	Ni(4)–O(72)	2.034(5)
Ni(5)···Ni(6)	3.301(9)	Ni(4)–O(91)	2.094(5)
Ni(1)–O(1)	2.057(5)	Ni(4)–OM(3)	2.095(6)
Ni(1)–O(71)	2.077(5)	Ni(4)–N(51)	2.070(8)
Ni(1)–O(82)	2.020(5)	Ni(4)–N(52)	2.082(7)
Ni(1)–OM(1)	2.108(6)	Ni(5)–O(11)	2.087(5)
Ni(1)–N(31)	2.069(7)	Ni(5)–O(61)	2.005(6)
Ni(1)–N(32)	2.067(6)	Ni(5)–O(81)	2.062(9)
Ni(2)–O(1)	2.081(5)	Ni(5)–O(102)	2.059(5)
Ni(2)–O(61)	2.016(6)	Ni(5)–N(1)	2.047(6)
Ni(2)–O(71)	2.135(5)	Ni(5)–N(2)	2.053(6)
Ni(2)–O(101)	2.077(5)	Ni(6)–O(21)	2.088(5)
Ni(2)–N(21)	2.065(6)	Ni(6)–O(61)	2.005(6)
Ni(2)–N(22)	2.047(6)	Ni(6)–O(91)	2.116(5)
Ni(3)–O(11)	2.067(5)	Ni(6)–O(103)	2.069(5)
Ni(3)–O(81)	2.070(5)	Ni(6)–N(11)	2.045(6)
Ni(3)–O(92)	2.032(5)	Ni(6)–N(12)	2.076(6)
O(1)–Ni(1)–OM(1)	173.6(2)	N(51)–Ni(4)–N(52)	78.3(3)
O(71)–Ni(1)–O(82)	89.7(2)	O(11)–Ni(5)–N(2)	177.2(2)
O(71)–Ni(1)–N(32)	169.2(2)	O(61)–Ni(5)–O(102)	93.0(2)
O(82)–Ni(1)–N(31)	168.0(2)	O(61)–Ni(5)–N(1)	167.8(3)
N(31)–Ni(1)–N(32)	78.1(3)	O(61)–Ni(5)–N(2)	89.8(2)
O(1)–Ni(2)–O(71)	78.36(19)	O(81)–Ni(5)–O(102)	167.2(2)
O(1)–Ni(2)–O(101)	89.17(19)	O(21)–Ni(6)–O(91)	78.15(18)
O(1)–Ni(2)–N(22)	176.4(2)	O(21)–Ni(6)–N(12)	177.3(2)
O(61)–Ni(2)–N(21)	167.1(3)	O(61)–Ni(6)–N(11)	167.2(3)
O(71)–Ni(2)–O(101)	166.8(2)	O(61)–Ni(6)–N(12)	89.9(2)
O(11)–Ni(3)–O(81)	80.46(18)	O(91)–Ni(6)–O(103)	166.20(19)
O(11)–Ni(3)–OM(2)	173.1(2)	Ni(1)–O(1)–Ni(2)	101.8(3)
O(81)–Ni(3)–N(41)	90.1(2)	Ni(1)–O(71)–Ni(2)	99.2(3)
O(81)–Ni(3)–N(42)	167.9(2)	Ni(2)–O(61)–Ni(5)	109.6(3)
O(92)–Ni(3)–N(41)	168.0(2)	Ni(2)–O(61)–Ni(6)	110.6(3)
O(21)–Ni(4)–OM(3)	171.0(2)	Ni(3)–O(11)–Ni(5)	100.4(3)
O(72)–Ni(4)–O(91)	90.3(2)	Ni(3)–O(81)–Ni(5)	99.6(3)
O(72)–Ni(4)–N(51)	171.0(2)	Ni(4)–O(21)–Ni(6)	102.0(3)
O(91)–Ni(4)–N(52)	169.2(3)	Ni(4)–O(91)–Ni(6)	100.1(3)



Table 3. Selected interatomic distances [Å] and angles [°] for one of the crystallographically independent hexanuclear molecules of complex  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$  ( $3\cdot 3\text{H}_2\text{O}$ ).

Ni(1)···Ni(2)	3.313(4)	Ni(3)–O(23)	2.013(3)
Ni(1)···Ni(3)	3.320(4)	Ni(3)–N(5)	2.066(4)
Ni(2)···Ni(3)	3.307(4)	Ni(3)–N(6)	2.061(3)
Ni(4)···Ni(5)	6.000(4)	Ni(4)–O(1)	2.089(3)
Ni(4)···Ni(6)	5.978(4)	Ni(4)–O(12)	2.034(3)
Ni(5)···Ni(6)	6.019(4)	Ni(4)–O(17)	2.109(3)
Ni(1)–O(2)	2.105(4)	Ni(4)–OW(24)	2.055(3)
Ni(1)–O(7)	2.070(3)	Ni(4)–N(7)	2.080(4)
Ni(1)–O(14)	2.109(3)	Ni(4)–N(8)	2.100(4)
Ni(1)–O(23)	2.023(3)	Ni(5)–O(3)	2.092(3)
Ni(1)–N(1)	2.070(4)	Ni(5)–O(18)	2.015(3)
Ni(1)–N(2)	2.069(4)	Ni(5)–O(21)	2.062(3)
Ni(2)–O(3)	2.084(3)	Ni(5)–OW(25)	2.157(4)
Ni(2)–O(9)	2.083(3)	Ni(5)–N(9)	2.050(8)
Ni(2)–O(21)	2.133(3)	Ni(5)–N(10)	2.004(8)
Ni(2)–O(23)	2.013(3)	Ni(6)–O(2)	2.083(3)
Ni(2)–N(3)	2.057(4)	Ni(6)–O(14)	2.101(4)
Ni(2)–N(4)	2.057(4)	Ni(6)–O(22)	2.003(4)
Ni(3)–O(1)	2.083(3)	Ni(6)–OW(26)	2.085(4)
Ni(3)–O(8)	2.081(3)	Ni(6)–N(11)	2.064(4)
Ni(3)–O(17)	2.116(3)	Ni(6)–N(12)	2.086(5)
O(2)–Ni(1)–N(2)	177.2(1)	N(7)–Ni(4)–N(8)	77.4(2)
O(7)–Ni(1)–O(14)	164.5(1)	O(3)–Ni(5)–OW(25)	175.2(2)
O(14)–Ni(1)–N(1)	93.0(2)	O(18)–Ni(5)–O(21)	88.9(2)
O(23)–Ni(1)–N(1)	166.1(2)	O(18)–Ni(5)–N(9)	169.0(3)
O(23)–Ni(1)–N(2)	88.7(1)	O(21)–Ni(5)–N(10)	165.5(3)
O(3)–Ni(2)–O(21)	77.9(1)	N(9)–Ni(5)–N(10)	78.5(3)
O(3)–Ni(2)–N(4)	177.4(1)	O(2)–Ni(6)–OW(26)	172.8(1)
O(9)–Ni(2)–O(21)	165.5(1)	O(14)–Ni(6)–N(12)	169.4(2)
O(21)–Ni(2)–N(4)	101.8(1)	O(22)–Ni(6)–N(11)	172.9(2)
O(23)–Ni(2)–N(3)	167.2(1)	OW(26)–Ni(6)–N(12)	87.9(2)
O(1)–Ni(3)–N(6)	177.5(1)	N(11)–Ni(6)–N(12)	78.1(2)
O(8)–Ni(3)–O(17)	166.9(1)	Ni(1)–O(23)–Ni(2)	110.3(2)
O(8)–Ni(3)–N(6)	91.8(1)	Ni(1)–O(23)–Ni(3)	110.7(2)
O(23)–Ni(3)–N(5)	167.1(1)	Ni(1)–O(2)–Ni(6)	102.6(2)
N(5)–Ni(3)–N(6)	78.7(1)	Ni(1)–O(14)–Ni(6)	101.8(2)
O(1)–Ni(4)–OW(24)	170.2(1)	Ni(2)–O(3)–Ni(5)	101.6(2)
O(12)–Ni(4)–N(7)	174.2(2)	Ni(2)–O(21)–Ni(5)	101.0(2)
O(17)–Ni(4)–N(7)	91.4(2)	Ni(3)–O(1)–Ni(4)	102.8(2)
O(17)–Ni(4)–N(8)	168.2(2)	Ni(3)–O(17)–Ni(4)	101.0(2)

Figure 3. Partially labelled plot of the hexanuclear molecule present in complex  $1\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$ . The hydrogen atoms have been omitted for clarity.

lar structures of the three complexes are similar in many aspects and, thus, only the structure of the representative complex  $1\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$  will be described in detail.

Table 4. Details for the intramolecular hydrogen bonds in complex  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3(\text{MeOH})_2\cdot (\text{H}_2\text{O})]\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$  ( $1\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$ ).<sup>[a]</sup>

D–H···A	D···A [Å]	H···A [Å]	DHA [°]
O(4)–H(O4)···O(11)	2.569	1.638	168.9
O(5)–H(O5)···O(15)	2.558	1.486	175.1
O(6)–H(O6)···O(19)	2.583	1.755	172.0
OM(26)–H(OM26)···O(13)	2.626	1.826	162.6
OW(24)–H(OW24)···O(16)	2.666	1.721	157.0
OM(25)–H(OM25)···O(20)	2.618	1.966	148.3
OM(30) <sup>[b]</sup> –H(OM30)···O(10)	2.658	1.588	162.8
OW(31) <sup>[c]</sup> –H(OW31)···O(13)	2.872	1.838	164.6
OW(24)–H(OW24)···OW(31)	2.725	1.760	167.2

[a] A = acceptor; D = donor. [b] Atom OM(30) [not shown in Figure 3] belongs to lattice methanol. [c] Atom OW(31) [not shown in Figure 3] belongs to lattice water.

Table 5. Details for the intramolecular hydrogen bonds in complex  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3(\text{MeOH})_3\cdot 3.2\text{MeOH}\cdot 1.5\text{H}_2\text{O} (2\cdot 3.2\text{MeOH}\cdot 1.5\text{H}_2\text{O})$ .<sup>[a]</sup>

D–H...A	D...A [Å]	H...A [Å]	DHA [°]
OM(1)–H(OM1)...O(73)	2.658	1.859	151.0
OM(2)–H(OM2)...O(83)	2.650	1.836	169.2
OM(3)–H(OM3)...O(94)	2.647	2.022	125.1
O(31)–H(O31)...O(84)	2.560	1.747	171.0
O(41)–H(O41)...O(93)	2.583	1.800	159.2

[a] A = acceptor; D = donor.

Table 6. Details for the intramolecular hydrogen bonds in one of the two crystallographically independent hexanuclear molecules of complex  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{ph})\text{NO}\}_3\{(\text{py})\text{C}(\text{ph})\text{NOH}\}_3\cdot (\text{H}_2\text{O})_3\cdot 3\text{H}_2\text{O} (3\cdot 3\text{H}_2\text{O})$ .<sup>[a]</sup>

D–H...A	D...A [Å]	H...A [Å]	DHA [°]
O(4)–H(O4)...O(13)	2.558(7)	1.77	154.6
O(5)–H(O5)...O(15)	2.654(8)	1.82	177.4
O(5A)–H(O5A)...O(15)	2.388(11)	1.59	157.1
O(6)–H(O6)...O(20)	2.547(8)	1.71	172.8
O(6)–H(O6)...O(20A)	2.468(11)	1.65	162.5
O(23)–H(O23)...O(22)	3.001(5)	2.46	123.6
O(23)–H(O23)...O(12)	3.134(3)	2.59	123.5

[a] A = acceptor; D = donor.

In the following the binding modes of the various ligands will be often described using Harris notation.<sup>[21]</sup> Occasionally we shall use the widely approved notation based on the Greek letters  $\mu$  and  $\eta$ .

Complex  $1\cdot 2.53\text{MeOH}\cdot 1.60\text{H}_2\text{O}$  crystallizes in the monoclinic space group  $P2_1/n$ . Its structure consists of hexanuclear  $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3(\text{MeOH})_2(\text{H}_2\text{O})]$  molecules, and MeOH and  $\text{H}_2\text{O}$  solvate molecules; the latter two will not be further discussed. If we assume that the nitrogen atoms of the  $\mu_3$  oximate groups and the terminal oxygen atoms of the 3.2100 sulfato ligands (Figure 4) contribute to the core formation, the molecule of **1** contains the  $[\text{Ni}_6(\mu_3\text{-OH})(\mu_3\text{-SO}_4)_3(\mu_3\text{-ONR})_3]^{2+}$  core; an alternative description of the core (using only the bridging oxygen atoms) is  $[\text{Ni}_6(\mu_3\text{-OH})(\mu\text{-OR}')_3(\mu\text{-OR}'')_3]^{2+}$ , where  $\text{R}' = \text{SO}_3$  and  $\text{R}'' = \text{NC}(\text{py})(\text{Me})$ . The topology of the core consists of six  $\text{Ni}^{\text{II}}$  ions arranged as two parallel (Figure 5), near-equilateral triangular subunits, one "small" and the other "large". The metal ions in the small triangle [defined by Ni(1), Ni(2) and Ni(3)] are held together by the  $\mu_3\text{-OH}^-$  ligand [O(23)] and one  $\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\mu_3$  (or 3.1110,<sup>[21]</sup> Figure 2) sulfato group. Each  $\text{Ni}_2$  edge is additionally bridged by one diatomic oximate group from one 3.211  $(\text{py})\text{C}(\text{Me})\text{NO}^-$  ligand (Figure 6). Each  $\text{Ni}_2$  edge of the large triangle [defined by Ni(4), Ni(5) and Ni(6)] is bridged by two oxygen atoms of one  $\eta^1\text{:}\eta^2\text{:}\mu_3$  (or 3.2100, Figure 4) sulfato ligand. Each apex of the small triangular unit is linked to an apex of the large triangular unit by two monoatomic oxygen bridges from one 3.2100  $\text{SO}_4^{2-}$  ion and one 3.211  $(\text{py})\text{C}(\text{Me})\text{NO}^-$  ligand, and to another apex of the large triangle by the diatomic oximate group of one 3.211 pyridyloximate ligand already used to bridge a  $\text{Ni}_2$  edge of the small triangle. One bidentate chelating  $(\text{py})\text{-}$

$\text{C}(\text{Me})\text{NOH}$  molecule (1.011, Figure 6) and one terminal solvate ligand [MeOH at Ni(5) and Ni(6),  $\text{H}_2\text{O}$  at Ni(4)] complete six-coordination at each metal center of the large triangle.

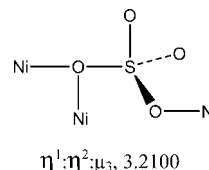


Figure 4. The new  $\eta^1\text{:}\eta^2\text{:}\mu_3$  (3.2100) coordination mode of the  $\text{SO}_4^{2-}$  ion which has been crystallographically identified in complexes **1–3**.

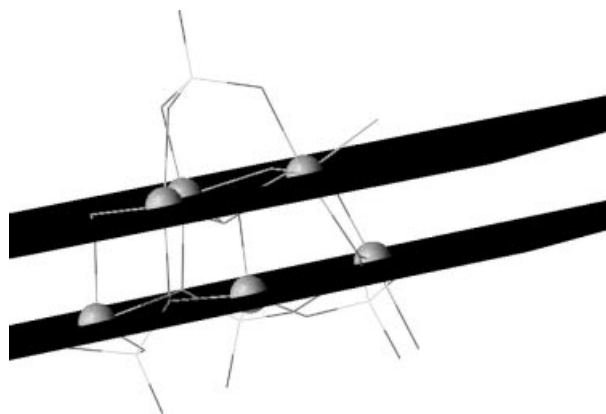


Figure 5. A view of **1** emphasizing the parallel  $\text{Ni}_3$  planes.

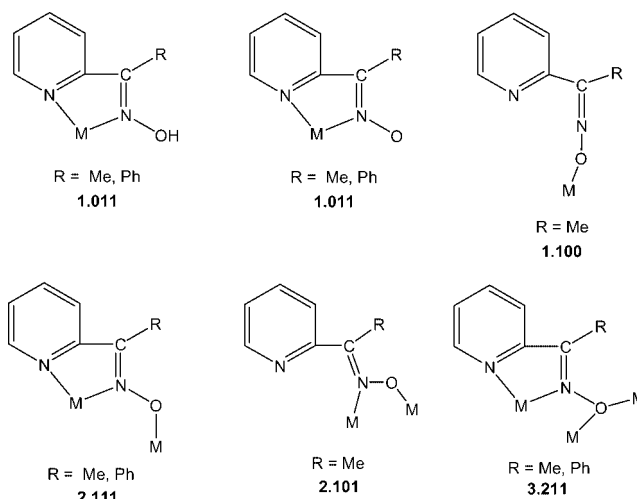


Figure 6. The up to now crystallographically established coordination modes of the ligands  $(\text{py})\text{C}(\text{ph})\text{NOH}$ ,  $(\text{py})\text{C}(\text{ph})\text{NO}^-$ ,  $(\text{py})\text{-C}(\text{Me})\text{NOH}$  and  $(\text{py})\text{C}(\text{Me})\text{NO}^-$ , and the Harris notation<sup>[21]</sup> that describes these modes. The 3.211 ligation mode of  $(\text{py})\text{C}(\text{Me})\text{NO}^-$  is new and has identified for the first time in complex **1**.

Using the perspective view of Figure 5, the  $\mu_3\text{-OH}$  oxygen atom O(23) is 0.633 Å below the  $\text{Ni}_3$  plane that it bridges  $[\text{Ni}(1)\text{Ni}(2)\text{Ni}(3)]$ , i.e. the hydroxido ligand is between the almost parallel planes (dihedral angle: 0.6°) defined by the two triangular subunits. The distance between the

planes is 2.182 Å. The small triangle can be viewed as an inverse 9-metallacrown-3 subunit.<sup>[9]</sup>

The Ni<sup>II</sup>...Ni<sup>II</sup> separations within the small triangular unit are in the narrow 3.293(4)–3.304(4) Å range; those within the large one are in the 5.947(4)–6.000(4) Å range. A distorted octahedral environment is created about each metal center. The Ni–O<sub>sulfato</sub> bond lengths are typical.<sup>[15c,18,22]</sup> The Ni–O bond lengths for the bridging sulfate oxygen atoms are longer than the Ni–O distance exhibited by the terminal oxygen atom from the same sulfato ligand.

There is a large amount of hydrogen bonding in 1·2.53 MeOH·1.60 H<sub>2</sub>O. We will briefly comment on the intramolecular hydrogen bonds, see Table 4. Each (py)C(Me)NOH oxime group is strongly intramolecularly hydrogen-bonded to an uncoordinated O atom from a 3.2100 sulfato ligand. The other uncoordinated O atom of each 3.2100 sulfato ligand also acts as acceptor; the donors for these hydrogen bonds are the MeOH and H<sub>2</sub>O ligands. The sulfato O(13) atom participates in two hydrogen bonds; of interest is also the fact that the lattice water oxygen atom OW(31) acts both as a donor and as an acceptor.

The structures of the hexanuclear molecules present in complexes 2·3.2 MeOH·1.5 H<sub>2</sub>O (Figure 7) and 3·3 H<sub>2</sub>O (Figure 8) are very similar to the structure of 1 except that: (i) The (py)C(Me)NOH/(py)C(Me)NO<sup>−</sup> ligands of 1 are replaced by (py)C(ph)NOH/(py)C(ph)NO<sup>−</sup> ligands in 2 and 3, and (ii) the peripheral MeOH and H<sub>2</sub>O ligands of 1 are replaced by three terminal MeOH ligands in 2 and three terminal H<sub>2</sub>O ligands in 3. Note that there are two crystallographically independent hexanuclear molecules in 3·3 H<sub>2</sub>O, but their bond lengths and angles differ only marginally. The three compounds also differ in the lattice solvate molecules that are present.

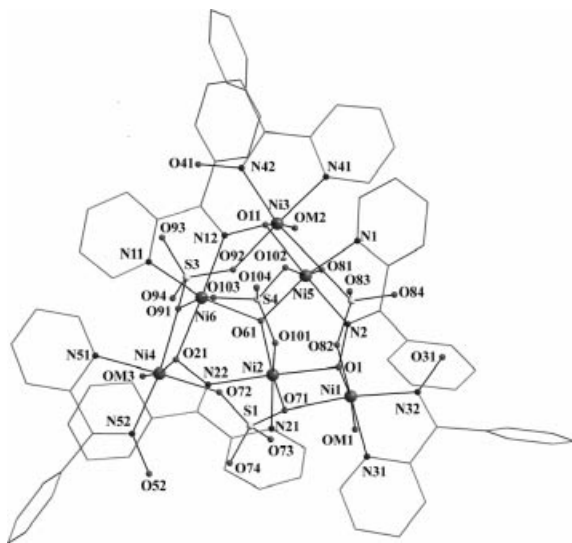


Figure 7. Partially labelled plot of the hexanuclear molecule present in complex 2·3.2 MeOH·1.5 H<sub>2</sub>O. The hydrogen atoms have been omitted for clarity.

The ligands (py)C(Me)NOH, (py)C(Me)NO<sup>−</sup>, (py)C(ph)NOH and (py)C(ph)NO<sup>−</sup> have been observed in numerous ligation modes over the years.<sup>[12]</sup> Because most of their

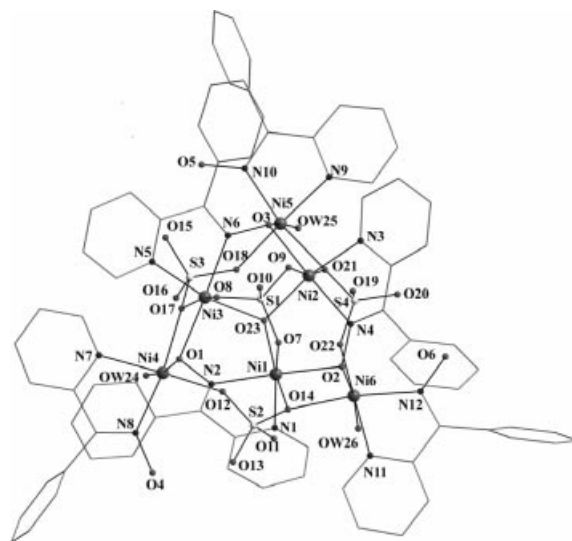


Figure 8. Partially labelled plot of one of the two, crystallographically independent hexanuclear molecules present in complex 3·3 H<sub>2</sub>O. The hydrogen atoms have been omitted for clarity.

complexes were reported only recently, we felt it timely to collect the structurally characterized non-organometallic, metal complexes of these ligands in Tables 7 and 8, together with the cores of the polynuclear complexes and the coordination modes of (py)C(R)NOH/(py)C(R)NO<sup>−</sup> (R = Me, Ph). Inspection of Tables 7 and 8 clearly shows that: (i) the complexes 1–3 are amongst the highest-nuclearity clusters of any metal identified with the (py)C(R)NO<sup>−</sup> ligands, (ii) the 2.111 coordination mode is the most common for the bridging (py)C(R)NO<sup>−</sup> ligands, and (iii) the 3.211 mode of (py)C(Me)NO<sup>−</sup> observed in 1 is new, i.e. it has not been characterized before, while this mode is rare in the complexes containing bridging (py)C(ph)NO<sup>−</sup> ligands.

Complexes 1–3 join a rather small, but growing family of Ni<sup>II</sup><sub>6</sub> complexes bearing N- and/or O-donors and possessing the metal ions in various topologies, such as hexagons, Chinese-lantern-like objects and face-shared distorted dicubanes in which one of the corners of each cubane is missing.<sup>[24]</sup> Complexes 1–3 are the highest-nuclearity sulfato nickel(II) clusters which have been structurally characterized.

## Magnetic Studies

Solid-state dc magnetic susceptibility measurements were performed on polycrystalline samples of the representative complexes 1 and 2, under a constant field of 0.04 T in the temperature range 2.0–300 K. The  $\chi_M T$  vs.  $T$  plots for the two complexes are shown in Figure 9. The complexes exhibit a very similar magnetic behavior. The  $\chi_M T$  values at room temperature are 7.39 cm<sup>3</sup> mol<sup>−1</sup> K for 1 and 7.50 cm<sup>3</sup> mol<sup>−1</sup> K for 2, close to the expected value of 7.59 cm<sup>3</sup> mol<sup>−1</sup> K for six non-interacting  $S = 1$  centers assuming  $g = 2.25$ . As the temperature is lowered, the  $\chi_M T$  product for both compounds experiences a slight decrease in the 300 to ca. 75 K range, followed by a sharper decline

Table 7. Formulae, coordination modes of the ligands and cores for the structurally characterized metal complexes of (py)C(Me)NOH and/or (py)C(Me)NO<sup>−</sup>.

Complex <sup>[a]</sup>	Coordination modes <sup>[b]</sup>	Core <sup>[c]</sup>	Ref.
[Mn <sup>III</sup> <sub>3</sub> O(O <sub>2</sub> CMe) <sub>3</sub> {(py)C(Me)NO} <sub>3</sub> ]	2.111	[Mn <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)] <sup>7+</sup>	[10h,10n]
[Mn <sup>III</sup> <sub>3</sub> O(O <sub>2</sub> CEt) <sub>3</sub> {(py)C(Me)NO} <sub>3</sub> ]	2.111	[Mn <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)] <sup>7+</sup>	[10h,10n]
<i>fac</i> -[Co <sup>III</sup> {(py)C(Me)NO} <sub>3</sub> ]	1.011		[14a]
[NiBr <sub>2</sub> {(py)C(Me)NOH} <sub>2</sub> ]	1.011		[23a]
[Ni{(py)C(Me)NO}{(py)C(Me)NOH}(H <sub>2</sub> O) <sub>2</sub> ] <sup>[d]</sup>	1.011, 1.011		[23a,23b]
[Ni <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH){(py)C(Me)NO} <sub>3</sub> {(py)C(Me)NOH} <sub>3</sub> (MeOH) <sub>2</sub> (H <sub>2</sub> O)]	3.211, 1.011	[Ni <sub>6</sub> (μ <sub>3</sub> -OH)(μ <sub>3</sub> -SO <sub>4</sub> ) <sub>3</sub> (μ <sub>3</sub> -ONR) <sub>3</sub> ] <sup>2+</sup> <sup>[e]</sup>	this work
[ZnCl <sub>2</sub> {(py)C(Me)NOH} <sub>2</sub> ]	1.011		[23c]
[Zn <sub>4</sub> (OH) <sub>2</sub> Cl <sub>2</sub> {(py)C(Me)NO} <sub>4</sub> ]	2.111	[Zn <sub>4</sub> (μ-OH) <sub>2</sub> ] <sup>6+</sup>	[23c]
[Zn(NO <sub>3</sub> ) <sub>2</sub> {(py)C(Me)NOH} <sub>2</sub> ]	1.011		[23d]
[Rh <sup>III</sup> Cl <sub>2</sub> {(py)C(Me)NO}{(py)C(Me)NOH}]	1.011, 1.011		[23e]
[Pt <sup>II</sup> {(py)C(Me)NO} <sub>2</sub> ]	1.011		[23f]
<i>n</i> Bu <sub>8</sub> Sn <sub>4</sub> O <sub>2</sub> {(py)C(Me)NO} <sub>4</sub>	1.100, 2.101	[Sn <sup>IV</sup> <sub>4</sub> (μ <sub>3</sub> -O) <sub>2</sub> ] <sup>12+</sup>	[23g]
[Et <sub>8</sub> Sn <sub>4</sub> O <sub>2</sub> {(py)C(Me)NO} <sub>4</sub> ]	1.100, 2.101	[Sn <sup>IV</sup> <sub>4</sub> (μ <sub>3</sub> -O) <sub>2</sub> ] <sup>12+</sup>	[23g]
[Me <sub>8</sub> Sn <sub>4</sub> O <sub>2</sub> {(py)C(Me)NO} <sub>4</sub> ]	1.100, 2.111	[Sn <sup>IV</sup> <sub>4</sub> (μ <sub>3</sub> -O) <sub>2</sub> ] <sup>12+</sup>	[23h]
[Ph <sub>3</sub> Sb{(py)C(Me)NO} <sub>2</sub> ]	1.100		[23i]

[a] Counterions and lattice solvent molecules have been omitted. [b] Using Harris notation<sup>[21]</sup> (see also Figure 6). [c] Only for the polynuclear complexes; the nitrogen atoms of the μ<sub>3</sub> oximate groups and the terminal oxygen atoms of the 3.2100 sulfato ligands are considered as contributors to the cores. [d] Both the nitrate and perchlorate salts have been structurally characterized. [e] Another representation of the core could be [Ni<sub>6</sub>(μ<sub>3</sub>-OH)(μ-OR')<sub>3</sub>(μ-OR'')<sub>3</sub>]<sup>2+</sup>, where R' = -SO<sub>3</sub> and R'' = -NC(py)(Me).

Table 8. Formulae, coordination modes of the ligands and cores for the structurally characterized metal complexes of (py)C(ph)NOH and/or (py)C(ph)NO<sup>−</sup>.

Complex <sup>[a]</sup>	Coordination modes <sup>[b]</sup>	Core <sup>[c]</sup>	Ref.
[Mn(O <sub>2</sub> CPh) <sub>2</sub> {(py)C(ph)NOH} <sub>2</sub> ]	1.011		[10c]
[Mn <sup>II</sup> <sub>4</sub> Mn <sup>III</sup> <sub>4</sub> (OH) <sub>2</sub> O <sub>2</sub> (O <sub>2</sub> CPh) <sub>10</sub> {(py)C(ph)NO} <sub>4</sub> ]	2.111	[Mn <sup>II</sup> <sub>4</sub> Mn <sup>III</sup> <sub>4</sub> (μ <sub>4</sub> -O) <sub>2</sub> (μ <sub>3</sub> -OH) <sub>2</sub> ] <sup>14+</sup>	[10c]
[Mn <sup>II</sup> <sub>3</sub> Mn <sup>IV</sup> O(N <sub>3</sub> )(O <sub>2</sub> CPh) <sub>3</sub> {(py)C(ph)NO} <sub>4</sub> ]	2.111	[Mn <sup>II</sup> <sub>3</sub> Mn <sup>IV</sup> (μ <sub>4</sub> -O)(η <sup>1</sup> : μ <sub>2</sub> -N <sub>3</sub> )] <sup>7+</sup>	[10i]
[Mn <sup>III</sup> <sub>3</sub> O(O <sub>2</sub> CMe) <sub>3</sub> {(py)C(ph)NO} <sub>3</sub> ]	2.111	[Mn <sup>III</sup> <sub>3</sub> (μ <sub>3</sub> -O)] <sup>7+</sup>	[10n]
[Co <sup>II</sup> Co <sup>III</sup> <sub>2</sub> {(py)C(ph)NO} <sub>6</sub> ] <sup>2+</sup>	2.111	[Co <sup>II</sup> Co <sup>III</sup> <sub>2</sub> (μ-ONR) <sub>6</sub> ] <sup>2+</sup>	[14a]
<i>mer</i> -[Co <sup>III</sup> {(py)C(ph)NO} <sub>3</sub> ]	1.011		[14a]
[Ni <sub>4</sub> (O <sub>2</sub> CMe) <sub>4</sub> {(py)C(ph)NO} <sub>4</sub> (MeOH) <sub>2</sub> ]	3.211	[Ni <sub>4</sub> (μ <sub>3</sub> -ONR) <sub>4</sub> ] <sup>4+</sup> <sup>[d]</sup>	[10p]
[Ni <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH){(py)C(ph)NO} <sub>3</sub> {(py)C(ph)NOH} <sub>3</sub> (MeOH) <sub>3</sub> ]	3.211, 1.011	[Ni <sub>6</sub> (μ <sub>3</sub> -OH)(μ <sub>3</sub> -SO <sub>4</sub> ) <sub>3</sub> (μ <sub>3</sub> -ONR) <sub>3</sub> ] <sup>2+</sup> <sup>[e]</sup>	this work
[Ni <sub>6</sub> (SO <sub>4</sub> ) <sub>4</sub> (OH){(py)C(ph)NO} <sub>3</sub> {(py)C(ph)NOH} <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ]	3.211, 1.011	[Ni <sub>6</sub> (μ <sub>3</sub> -OH)(μ <sub>3</sub> -SO <sub>4</sub> ) <sub>3</sub> (μ <sub>3</sub> -ONR) <sub>3</sub> ] <sup>2+</sup> <sup>[e]</sup>	this work

[a] Counterions and lattice solvent molecules have been omitted. [b] Using Harris notation<sup>[21]</sup> (see also Figure 6). [c] Only for the polynuclear complexes; the nitrogen atoms of the μ<sub>3</sub> oximate groups and the terminal oxygen atoms of the 3.2100 sulfato ligands are considered as contributors to the cores. [d] Another representation of the core could be [Ni<sub>4</sub>(μ-OR')<sub>4</sub>]<sup>4+</sup>. [e] Another representation of the core could be [Ni<sub>6</sub>(μ<sub>3</sub>-OH)(μ-OR')<sub>3</sub>(μ-OR'')<sub>3</sub>]<sup>2+</sup>, where R' = SO<sub>3</sub> and R'' = NC(py)(ph).

at lower temperatures and reaching the values of 2.37 (**1**) and 3.14 (**2**) cm<sup>3</sup>mol<sup>−1</sup> K at 2.0 K. The data indicate an overall antiferromagnetic behavior. Magnetization experiments performed at 2.0 K (Figure 10) show a continuous

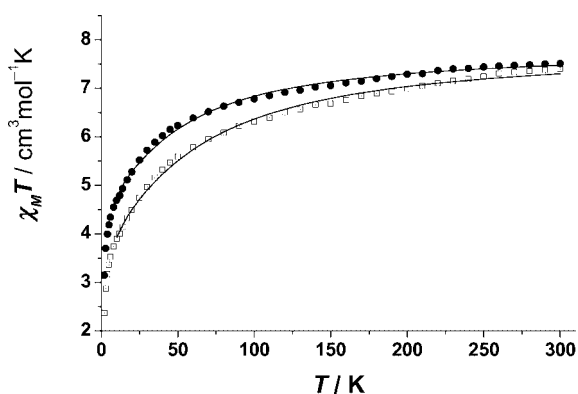


Figure 9.  $\chi_M T$  vs.  $T$  plots for complexes **1** (open squares) and **2** (open circles). The solid lines represent the best fit to the data as described in the text.

increase of  $M$  as the field increases, reaching a non-saturated value close to five electrons under an external field of 5 T.

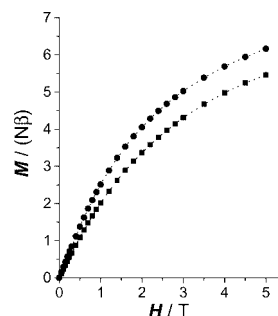


Figure 10. Magnetization plots for compounds **1** (filled squares) and **2** (filled circles) at 2 K. The dashed lines are guides for the eye.

Close inspection of the very similar molecular structures reveals that there are four different superexchange pathways and thus four different kinds of  $J$  values:  $J_1$  is associated (from now onwards the numbering scheme that will be used



is the same with that used in the real structure of **1**, see Figure 3) with the Ni(1)⋯Ni(2), Ni(2)⋯Ni(3) and Ni(1)⋯Ni(3) interactions through the central hydroxido bridge, a triatomic part of the 3.1110 sulfato ligand and one diatomic oximate group from a 3.211 (py)C(Me)NO<sup>−</sup> ligand;  $J_2$  is associated with the Ni(1)⋯Ni(6), Ni(2)⋯Ni(5) and Ni(3)⋯Ni(4) interactions, each through a double (μ-O<sub>sulfato</sub>)/(μ-O<sub>oximate</sub>) pathway;  $J_3$  is associated with the Ni(1)⋯Ni(4), Ni(2)⋯Ni(6) and Ni(3)⋯Ni(5) interactions, each through one diatomic oximate group from a 3.211 (py)C(Me)NO<sup>−</sup> ligand (the Ni–O–N–Ni torsion angles are close to 90°); and finally  $J_4$  is associated with the Ni(4)⋯Ni(5), Ni(5)⋯Ni(6) and Ni(4)⋯Ni(6) interactions, each through a single triatomic part of one 3.2100 sulfato ligand. If we consider that the six Ni<sup>II</sup> ions occupy the apices of a very distorted octahedron, the superexchange pathways are along the twelve edges. The spin Hamiltonian for such a system is given by Equation (1).

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) - J_2(S_1 \cdot S_6 + S_2 \cdot S_5 + S_3 \cdot S_4) - J_3(S_1 \cdot S_4 + S_2 \cdot S_6 + S_3 \cdot S_5) \quad (1)$$

$$H = -J_4(S_4 \cdot S_5 + S_4 \cdot S_6 + S_5 \cdot S_6)$$

To avoid a vast parameterization, we decided to attempt to fit the susceptibility data using a simpler 2- $J$  model. In order to decide the best way to reduce the number of the coupling constants, we have performed the following analysis of the above mentioned “octahedral” model. It is known that the superexchange Ni–O–X–O–Ni interactions mediated by tetrahedral anions with electronegative central atoms, e.g. SO<sub>4</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup>, PO<sub>4</sub><sup>3−</sup>, are negligible.<sup>[18]</sup> Assuming  $J_4 = 0$ , the spin Hamiltonian can be expressed in the form of Equation (2) and the resulting new, simpler interaction scheme is shown in Figure 11. In Figure 12 we show some selected simulations of the magnetic response of the “octahedral” model, performed by means of the program CLUMAG.<sup>[25]</sup>

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) - J_2(S_1 \cdot S_6 + S_2 \cdot S_5 + S_3 \cdot S_4) - J_3(S_1 \cdot S_4 + S_2 \cdot S_6 + S_3 \cdot S_5) \quad (2)$$

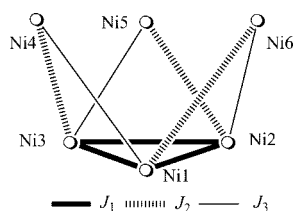


Figure 11. A 3- $J$  exchange-interaction pattern corresponding to the Hamiltonian of Equation (2) for the hexanuclear clusters reported in this work. The Hamiltonian of Equation (3) follows the same scheme assuming  $J_2 = J_3$ . The exchange pathways corresponding to  $J_1$ ,  $J_2$  and  $J_3$  are described in the text. The numbering scheme used for the Ni<sup>II</sup> ions is the same with that used in the solution of the structure of **1**·2.53 MeOH·1.60 H<sub>2</sub>O. Atoms Ni(1), Ni(2), Ni(3), Ni(4), Ni(5) and Ni(6) of the shown interaction scheme correspond to atoms Ni(2), Ni(6), Ni(5), Ni(4), Ni(3) and Ni(1), respectively, of the structure of **2**·3.2 MeOH·1.5 H<sub>2</sub>O (Figure 7).

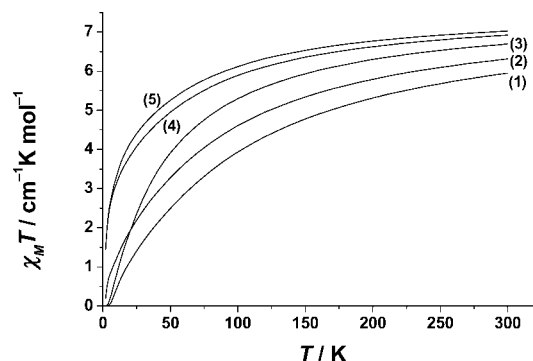


Figure 12. Calculated  $\chi_M T$  vs.  $T$  curves for a spin system similar to that of **1–3** and for various sets of the  $J$  constants. A detailed description of the curves (1)–(5) is given in the text.

Curve (1) represents the behavior of a system on the basis of the Hamiltonian of Equation (1) in the case of  $J_1 = J_2 = J_3 = J_4 = -20$  cm<sup>−1</sup> and  $g = 2.25$ . This system has a well-defined  $S = 0$  ground state as can be seen in Figure 13. Removing the interaction in one of the octahedral faces, i.e.  $J_4 = 0$ , with  $J_1 = J_2 = J_3 = -20$  cm<sup>−1</sup> and  $g = 2.25$ , and applying the Hamiltonian of Equation (2), we obtained curve (2); the system has a new  $S = 0$  ground state (Figure 13). Curve (3) of Figure 12 is the result of the calculation with the parameters  $J_1 = -20$  cm<sup>−1</sup>,  $J_2 = -10$  cm<sup>−1</sup>,  $J_3 = -5$  cm<sup>−1</sup> and  $g = 2.25$ . Again the system has an  $S = 0$  ground state (Figure 13). As it is clearly evident in Figure 12, in these three cases the  $\chi_M T$  value tends to zero at low temperatures by contrast with the experimental behavior of **1** and **2**, see Figure 9. More interesting are plots/curves (4) and (5) of Figure 12, obtained applying the sets  $J_1 = -20$  cm<sup>−1</sup>,  $J_2 = -5$  cm<sup>−1</sup>,  $J_3 = -5$  cm<sup>−1</sup> and  $J_1 = -20$  cm<sup>−1</sup>,  $J_2 = -5$  cm<sup>−1</sup>,  $J_3 = 0$  cm<sup>−1</sup>, respectively. For these simulations in which  $J_1 \gg J_2, J_3$ , the  $\chi_M T$  product does not strongly tend to zero at low temperatures (in agreement with the experimental data, see Figure 9); this is a consequence of the close “distances” of the  $S = 0, 1, 2, 3$  states in the energy spectrum, see Figure 13 for the  $J_1 = -20$  cm<sup>−1</sup>,  $J_2 = -5$  cm<sup>−1</sup>,  $J_3 = -5$  cm<sup>−1</sup> case, plot (4). It is important to realize that the relative values of  $J_2$  and  $J_3$  become poorly relevant and it is not reliable to try to fit separately these two coupling constants. It should be mentioned at this point that any calculation assuming  $J_1 \ll J_2, J_3$  gives  $\chi_M T$  products that clearly tend to a value close to zero, and such a situation can not be assumed for **1** and **2**.

On the basis of the above calculations, we decided to apply the spin Hamiltonian of Equation (3), where  $J_1$  is the coupling constant for the interactions within the small triangle [defined by Ni(1), Ni(2) and Ni(3) in **1**] and  $J_2$  is a common coupling constant associated with the six interactions between the small triangle and the three peripheral Ni<sup>II</sup> ions [Ni(4), Ni(5) and Ni(6) in **1**]. The best-fit parameters are  $J_1 = -20.5$  cm<sup>−1</sup>,  $J_2 = -2.3$  cm<sup>−1</sup>,  $g = 2.29$  for **1** and  $J_1 = -17.0$  cm<sup>−1</sup>,  $J_2 = -1.9$  cm<sup>−1</sup>,  $g = 2.30$  for **2**. The agreement factor, defined as  $R = \sum[(\chi_M)_{\text{calcd.}} - (\chi_M)_{\text{obsd.}}]^2 / \sum[(\chi_M)_{\text{obsd.}}]^2$  was  $1.1 \times 10^{-4}$  and  $8.1 \times 10^{-5}$  for **1** and **2**, respectively, see Figure 9. Looking at the energy of the  $S =$

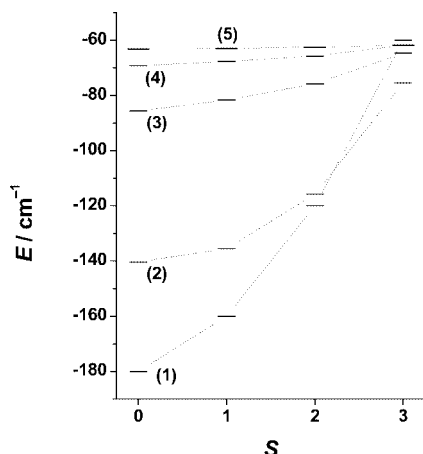


Figure 13. Energy levels for the  $S = 0, 1, 2, 3$  states in the following cases: Plot (1) refers to  $J_1 = J_2 = J_3 = J_4 = 20 \text{ cm}^{-1}$ ; plot (2) refers to  $J_1 = J_2 = J_3 = -20 \text{ cm}^{-1}$ ; plot (3) refers to  $J_1 = -20 \text{ cm}^{-1}$ ,  $J_2 = -10 \text{ cm}^{-1}$ ,  $J_3 = -5 \text{ cm}^{-1}$ ; plot (4) refers to  $J_1 = -20 \text{ cm}^{-1}$ ,  $J_2 = -5 \text{ cm}^{-1}$ ,  $J_3 = -5 \text{ cm}^{-1}$ ; plot (5) refers to  $J_1 = -20.5 \text{ cm}^{-1}$ ,  $J_2 = J_3 = -2.3 \text{ cm}^{-1}$ ,  $g = 2.29$ , set of parameters resulting from the fitting procedure for **1** based on the Hamiltonian of Equation (3).

0, 1, 2, 3 levels [plot (5) in Figure 13], we realize that these spin levels are very close, i.e. with a very narrow range of less than  $1.5 \text{ cm}^{-1}$ , in good agreement with the magnetization data (Figure 10). Upon increasing the external field, the close non-zero spin levels give a non-saturated magnetization at 2 K as a result of the partial population of levels up to  $S = 3$ . The next lower  $S = 4$  level is  $26 \text{ cm}^{-1}$  higher in energy, excluding a magnetization corresponding to more than six unpaired electrons, as it is experimentally observed.

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3 + S_2 \cdot S_3) - J_2(S_1 \cdot S_6 + S_2 \cdot S_5 + S_3 \cdot S_4 + S_1 \cdot S_4 + S_2 \cdot S_6 + S_3 \cdot S_5) \quad (3)$$

The bridging  $=\text{N}-\text{O}^-$  group is known to be very efficient in mediating a strong antiferromagnetic interaction, which is provided by an orbital exchange pathway essentially of  $\sigma$  nature.<sup>[14c]</sup> The antiferromagnetic  $J_1$  coupling is consistent with its mediation mainly by two types of bridges, a single-atom  $\mu_3\text{-OH}^-$  group with a  $\text{Ni}-\text{O}(\text{H})-\text{Ni}$  angle of ca.  $110^\circ$  and a diatomic  $=\text{N}-\text{O}^-$  linkage. The non-planarity of the  $\text{Ni}-\text{O}-\text{N}-\text{Ni}$  moiety (noticeable torsion angle) reduces the antiferromagnetism, giving rise to moderate antiferromagnetic coupling.<sup>[24b]</sup> The sign of  $J_2$  seems logical owing to its mediation by a  $(\mu\text{-O})_2$  pathway with an average  $\text{Ni}-\text{O}-\text{Ni}$  angle of ca.  $101^\circ$  and one diatomic, non-planar  $=\text{N}-\text{O}^-$  linkage; however, its magnitude can not be easily rationalized in the simple 2- $J$  model adopted.

## Conclusions and Perspectives

The initial use of the sulfate ligand in nickel(II)/2-pyridyl oximes chemistry, i.e. the study of the coordination chemistry of the *binary*  $\text{SO}_4^{2-}/(\text{py})\text{C}(\text{R})\text{NOH}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) “ligand blends” with nickel(II), has provided access to three hexanuclear clusters with interesting structures and magnetic

features. The magnetic properties of two representative clusters have been interpreted using two exchange interactions in a simplified model.

Analogues of **1–3** with 2-pyridinecarbaldehyde oxime  $[(\text{py})\text{C}(\text{H})\text{NOH}]$  or di-2-pyridyl ketone oxime  $[(\text{py})_2\text{CNOH}]$ , see Figure 1, are not known, until to date, and it is currently not evident whether the preparation and stability of such hexanuclear complexes are dependent on the particular nature of the R substituent on the oxime/oximate carbon. Clearly the  $\text{Ni}^{\text{II}}/\text{SO}_4^{2-}/(\text{py})\text{C}(\text{R})\text{NOH}$  chemistry warrants further study and expansion to other 3d-metals. Synthetic efforts are also in progress to realize a higher bridging behavior of the  $\text{SO}_4^{2-}$  ion, e.g.  $\mu_4\text{-}\mu_6$  (Figure 2) in 3d-metal/ $(\text{py})\text{C}(\text{R})\text{NOH}$  chemistry. Because the  $\mu_3\text{-OH}^-$  ligand propagates antiferromagnetic exchange interactions in the small  $\text{Ni}_3$  triangular unit of **1–2**, we are intensively pursuing our efforts to substitute the hydroxido bridge by an end-on triply bridging azido ligand ( $\eta^1\text{:}\mu_3$  or 3.100), according to our well-developed synthetic strategy,<sup>[26]</sup> in order to introduce specifically ferromagnetic components in the superexchange Scheme. Work at the time of writing shows that most of the just mentioned perspectives are realizable.

## Experimental Section

**Materials and Physical Measurements:** All manipulations were performed under aerobic conditions using materials and solvents (Merck, Aldrich) as received. Complex  $[\text{Ni}(\text{SO}_4)\{(\text{py})\text{C}(\text{Me})\text{NOH}\}(\text{H}_2\text{O})_3]$  was prepared as described elsewhere.<sup>[19]</sup> Methyl 2-pyridyl ketone oxime,  $(\text{py})\text{C}(\text{Me})\text{NOH}$ , was synthesized by the reaction of equimolar quantities of 1-pyridin-2-ylethanone (2-acetylpyridine),  $(\text{py})\text{C}(\text{Me})\text{O}$ ,  $\text{H}_2\text{NOH}\cdot\text{HCl}$  and  $\text{NaOEt}$  in  $\text{EtOH}$ .<sup>[27]</sup> Elemental analyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory with an EA 1108 Carlo-Erba analyzer. IR spectra ( $4000\text{--}400 \text{ cm}^{-1}$ ) were recorded with a Perkin-Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets. Magnetic susceptibility measurements in the 1.9–300 K range under a field of 0.5 T were performed with a Quantum Design SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were carried out on polycrystalline samples. Data were corrected for diamagnetic contributions using Pascal's constants.

**$[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3(\text{MeOH})_2(\text{H}_2\text{O})\} \cdot 2.53 \text{ MeOH} \cdot 1.60 \text{ H}_2\text{O}$  (**1**·2.53 MeOH·1.60 H<sub>2</sub>O). Method A:** Solid NaOMe (0.033 g, 0.60 mmol) was added to a colorless solution of  $(\text{py})\text{C}(\text{Me})\text{NOH}$  (0.082 g, 0.60 mmol) in MeOH (25 mL); the solid soon dissolved. Solid  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (0.158 g, 0.60 mmol) was then added and the resultant solution was stirred for 1 h at room temperature. A small quantity of undissolved material was removed by filtration and the green filtrate layered with  $\text{Et}_2\text{O}$  (50 mL). Slow mixing gave X-ray quality green crystals of the product. The crystals were collected by filtration, washed with cold  $\text{H}_2\text{O}$  (1 mL), cold MeOH (2 mL) and ice-cold  $\text{Et}_2\text{O}$  ( $2 \times 3 \text{ mL}$ ), and dried in air. Yield: 0.114 g (65%). The air-dried solid analyzed satisfactorily as MeOH-free (**1**·1.60 H<sub>2</sub>O).  $\text{C}_{44}\text{H}_{59.20}\text{N}_{12}\text{Ni}_6\text{O}_{27.60}\text{S}_4$  (1678.34): calcd. C 31.79, H 3.59, N 10.11; found C 31.45, H 3.72, N 9.98. IR data (KBr pellet):  $\tilde{\nu} = 3430$  (sh), 3406 (m, broad), 1652 (m), 1602 (s), 1562 (w), 1476 (m), 1440 (w), 1376 (w), 1334 (w), 1148 (s), 1126 (s), 1070 (s), 1036 (s), 984 (m), 782 (m), 690 (m), 628 (m), 592 (w), 484 (w), 430 (w)  $\text{cm}^{-1}$ .

**Method B:** A colorless solution of (py)C(Me)NOH (0.136 g, 1.00 mmol) in MeOH (10 mL) was slowly added to a slurry of LiOH·H<sub>2</sub>O (0.042 g, 1.00 mmol) in MeOH (5 mL); the hydroxide soon dissolved. The solution was then added to a slurry of NiSO<sub>4</sub>·6H<sub>2</sub>O (0.263 g, 1.00 mmol) in MeOH (10 mL) and the resulting green solution was stirred for 1 h at room temperature. A small quantity of undissolved material was removed by filtration. The filtrate was allowed to stand undisturbed in a closed flask for a period of 4–5 d. Green crystals appeared which were collected by filtration, washed with cold H<sub>2</sub>O (1 mL), cold MeOH (1 mL) and ice-cold Et<sub>2</sub>O (2 mL), and dried in air. Yield: 0.123 g (42%). The dried solid was analyzed satisfactorily as 1·1.60H<sub>2</sub>O. The identity of the product was further confirmed by IR spectroscopic comparison with the authentic sample prepared by method A.

**Method C:** A suspension of compound [Ni(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(Me)NOH}(H<sub>2</sub>O)<sub>3</sub>] (0.080 g, 0.22 mmol) in warm MeOH (25 mL) was treated with solid LiOH·H<sub>2</sub>O (0.006 g, 0.15 mmol). The mixture was stirred overnight at 30 °C, filtered to remove a few quantity of undissolved starting material, and the green solution was then allowed to stand undisturbed in a closed vial at room temperature. Green prismatic crystals formed within 12–14 h, and these were collected by filtration, washed with cold MeOH (2 × 2 mL) and dried in the air. Yield (based on the mononuclear complex): 0.026 g

(40%). The product was identified by microanalyses and IR comparison with material from method A.

**[Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(ph)NO}<sub>3</sub>{(py)C(ph)NOH}<sub>3</sub>(MeOH)<sub>3</sub>·3.2MeOH·1.5H<sub>2</sub>O (2·3.2MeOH·1.5H<sub>2</sub>O) and [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(ph)NO}<sub>3</sub>{(py)C(ph)NOH}<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>·3H<sub>2</sub>O (3·3H<sub>2</sub>O) as a Mixture:** Solid NaOMe (0.033 g, 0.60 mmol) was added to a colorless solution of (py)C(ph)NOH (0.119 g, 0.60 mmol) in MeOH (25 mL); the solid soon dissolved. Solid NiSO<sub>4</sub>·6H<sub>2</sub>O (0.158 g, 0.60 mmol) was then added and the resulting solution was stirred for 1 h at room temperature. A small quantity of undissolved material was removed by filtration and the orange filtrate layered with Et<sub>2</sub>O (50 mL). Slow mixing gave an approximately 1:1 mixture of greenish yellow prisms and yellow plates. The crystals were carefully collected by filtration, washed with cold H<sub>2</sub>O (0.5 mL), cold MeOH (1 mL) and ice-cold Et<sub>2</sub>O (2 × 3 mL), and dried in air. The two products were readily separable manually, and the yellow prisms and yellow plates proved by single-crystal X-ray crystallography to be complexes 2·3.2MeOH·1.5H<sub>2</sub>O and 3·3H<sub>2</sub>O, respectively. Batches of the different samples were used for analyses and characterization. Yield for 2·3.2MeOH·1.5H<sub>2</sub>O: 0.065 g (30%). The air-dried solid was analyzed satisfactorily as MeOH-free (2·1.5H<sub>2</sub>O). C<sub>75</sub>H<sub>73</sub>N<sub>12</sub>Ni<sub>6</sub>O<sub>27.5</sub>S<sub>4</sub> (2059.96): calcd. C 43.67, H 3.57, N 8.15; found C 43.23, H 3.72, N 7.91. IR data (KBr pellet)

Table 9. Crystal data and structure refinement for [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(Me)NO}<sub>3</sub>{(py)C(Me)NOH}<sub>3</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)]·2.53MeOH·1.60H<sub>2</sub>O (1·2.53MeOH·1.60H<sub>2</sub>O), [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(ph)NO}<sub>3</sub>{(py)C(ph)NOH}<sub>3</sub>(MeOH)<sub>3</sub>·3.2MeOH·1.5H<sub>2</sub>O (2·3.2MeOH·1.5H<sub>2</sub>O) and [Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(ph)NO}<sub>3</sub>{(py)C(ph)NOH}<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>·3H<sub>2</sub>O (3·3H<sub>2</sub>O)].

	1·2.53 MeOH·1.60 H <sub>2</sub> O	2·3.2 MeOH·1.5 H <sub>2</sub> O	3·3 H <sub>2</sub> O
Empirical formula	C <sub>46.53</sub> H <sub>69.32</sub> N <sub>12</sub> Ni <sub>6</sub> O <sub>30.13</sub> S <sub>4</sub>	C <sub>78.20</sub> H <sub>85.80</sub> N <sub>12</sub> Ni <sub>6</sub> O <sub>30.70</sub> S <sub>4</sub>	C <sub>72</sub> H <sub>70</sub> N <sub>12</sub> Ni <sub>6</sub> O <sub>29</sub> S <sub>4</sub>
Mol. mass	1759.40	2165.49	2047.90
Colour and habit	green prisms	yellow prisms	yellow plates
Crystal size [mm]	0.09 × 0.15 × 0.17	0.15 × 0.35 × 0.75	0.03 × 0.11 × 0.11
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Cc</i>
<i>a</i> [Å]	12.639(1)	30.941(18)	29.854(2)
<i>b</i> [Å]	41.824(2)	17.235(9)	17.358(12)
<i>c</i> [Å]	13.223(1)	23.649(13)	33.731(2)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	102.95(1)	97.24(2)	96.43(2)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	6811.8(7)	12511(12)	17370(2)
<i>Z</i>	4	4	8
<i>ρ</i> <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.714	1.150	1.566
<i>T</i> [°C]	−173(2)	25	−80(2)
<i>λ</i> [Mo- <i>K</i> <sub>α</sub> ] [Å]	0.71073		
Synchrotron [Å]			0.77490
<i>λ</i> [Cu- <i>K</i> <sub>α</sub> ] [Å]		1.54180	
<i>μ</i> [mm <sup>-1</sup> ]	1.840	2.140	1.835
<i>F</i> (000)	3616	4466	8400
2 $\theta$ <sub>max</sub> [°]	50.06	101.36	67.30
Index ranges	−15 ≤ <i>h</i> ≤ 14 −46 ≤ <i>k</i> ≤ 49 −15 ≤ <i>l</i> ≤ 15	−31 ≤ <i>h</i> ≤ 29 −17 ≤ <i>k</i> ≤ 0 0 ≤ <i>l</i> ≤ 23	−42 ≤ <i>h</i> ≤ 42 −24 ≤ <i>k</i> ≤ 22 −47 ≤ <i>l</i> ≤ 48
No. of reflections collected	33882	13070	95514
No. of independent reflections/ <i>R</i> <sub>int</sub>	11105/0.0540	12673/0.0178	51324/0.0338
Data with <i>I</i> > 2σ( <i>I</i> )	7069	9308	49155
Parameters refined	984	1171	2219
[Δ/ <i>σ</i> ] <sub>max</sub>	0.000	0.003	0.001
GOF (on <i>F</i> <sup>2</sup> )	0.938	1.055	1.106
[ <i>R</i> <sub>1</sub> ] <sup>[a]</sup>	0.0461	0.0729	0.0534
<i>wR</i> <sub>2</sub> <sup>[b]</sup>	0.0825	0.1988	0.1514
Residuals [e Å <sup>-3</sup> ]	1.068/−0.525	0.774/−0.644	1.149/−1.101

[a] *R*<sub>1</sub> = Σ(|*F*<sub>o</sub>| − |*F*<sub>c</sub>|)/Σ(|*F*<sub>o</sub>|). [b] *wR*<sub>2</sub> = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)/Σ(*w*(*F*<sub>o</sub><sup>2</sup>))]<sup>1/2</sup>.



for  $2 \cdot 1.5\text{H}_2\text{O}$ :  $\tilde{\nu}$  = 3415 (sh), 3396 (m, broad), 1599 (m), 1470 (m), 1442 (m), 1341 (w), 1180 (s), 1129 (s), 1051 (s), 1028 (s), 965 (m), 792 (m), 745 (m), 706 (m), 628 (m), 595 (w), 474 (w), 432 (w)  $\text{cm}^{-1}$ . Yield for  $3 \cdot 3\text{H}_2\text{O}$ : 0.073 g (35%).  $\text{C}_{72}\text{H}_{70}\text{N}_{12}\text{Ni}_6\text{O}_{29}\text{S}_4$  (2047.90): calcd. C 43.37, H 3.24, N 8.43; found C 43.45, H 3.14, N 8.50. IR data (KBr pellet) for  $3 \cdot 3\text{H}_2\text{O}$ :  $\tilde{\nu}$  = 3401 (sh), 3255 (m, broad), 1604 (m), 1466 (m), 1442 (m), 1337 (w), 1175 (s), 1125 (s), 1048 (s), 1028 (s), 971 (m), 788 (m), 746 (m), 704 (m), 627 (m), 598 (w), 468 (m), 429 (w)  $\text{cm}^{-1}$ .

**[Ni<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH){(py)C(ph)NO<sub>3</sub>}{(py)C(ph)NOH}<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>}]·3H<sub>2</sub>O (3·3H<sub>2</sub>O):** This complex was prepared pure in the form of yellow plates in a manner analogous to the above mentioned mixture, but using LiOH·H<sub>2</sub>O (0.017 g, 0.40 mmol) in place of NaOMe and MeOH/H<sub>2</sub>O (25 mL, 8:2, v/v) instead of MeOH. The yield was 0.001 g (60%). The air-dried solid analyzed satisfactorily as 3·3H<sub>2</sub>O. The identity of the product was further confirmed by unit cell determinations of three crystals. The three individual determinations revealed a unit cell with dimensions identical to those found for the yellow plates, which resulted from the above described procedure that led to the mixture of  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  and  $3 \cdot 3\text{H}_2\text{O}$ .

**X-ray Crystallographic Studies:** Crystals of  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  were mounted in Paratone-N oil, crystals of  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  in capillary filled with drops of mother liquor and crystals of  $3 \cdot 3\text{H}_2\text{O}$  were mounted in air at low temperature. Diffraction measurements for  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  were made with an Oxford Diffraction CCD instrument using graphite-monochromated Mo radiation. The X-ray data set for  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  was collected with a  $P_21$  Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu- $K_\alpha$  radiation, while diffraction measurements for  $3 \cdot 3\text{H}_2\text{O}$  were made with a Bruker Platinum 200 CCD diffractometer on Station 113.1<sup>[28a]</sup> of the Advanced Light Source at Lawrence Berkeley National Laboratory, with wavelength on 0.77490 Å from a Silicon 111 monochromator. Complete crystal data and parameters for data collection and refinement are listed in Table 9. Unit cell dimensions were determined and refined by using 10130 (for  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  at 100 K), 25 (for  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  at 298 K) and 8475 (for  $3 \cdot 3\text{H}_2\text{O}$  at 193 K) reflections in the ranges  $10.44 < 2\theta < 55.66^\circ$ ,  $22 < 2\theta < 54^\circ$  and  $5.10 < 2\theta < 67.30^\circ$ , respectively. The crystals of  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  had poor diffraction ability (despite their sufficient size) and the data were collected in increasing  $2\theta$  shells. The data collection was terminated when about 50% of the collected shell data were unobserved. The structures were solved by direct methods using SIR92<sup>[28b]</sup> ( $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$ ), SHELXS-86<sup>[28c]</sup> ( $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ ) and Bruker SHELXTL<sup>[28d]</sup> ( $3 \cdot 3\text{H}_2\text{O}$ ), and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[28e]</sup> (for  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  and  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ ) and Bruker SHELXTL<sup>[28d]</sup> (for  $3 \cdot 3\text{H}_2\text{O}$ ). For all the structures the fully occupied non-hydrogen atoms were refined anisotropically. In the case of  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  all lattice solvent molecules were refined with partial occupation factors, while in the case of  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$  the solvate molecules were refined isotropically. For the three structures, the hydrogen atoms attached to carbon atoms were placed at calculated positions. In  $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$  most other hydrogen atoms were located from  $\Delta F$  maps and refined isotropically. In  $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ , the hydroxy hydrogen atoms of the coordinated MeOH molecules and the hydrogen atom of the bridging hydroxido ligand were located by difference maps and refined isotropically. In the structure of  $3 \cdot 3\text{H}_2\text{O}$ , the bridging hydroxido hydrogen atom was found in the difference map, while hydrogen atoms could neither be found

or placed for the H<sub>2</sub>O molecules and were therefore omitted from the refinement.

CCDC-633009 ( $1 \cdot 2.53\text{MeOH} \cdot 1.60\text{H}_2\text{O}$ ), -633010 ( $2 \cdot 3.2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ ) and -633011 ( $3 \cdot 3\text{H}_2\text{O}$ ) 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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