

Note

Enneanuclear Ni(II) complexes from the use of the flexible ligand 2-pyridinealdoxime: The nature of the inorganic anion does not affect the chemical and structural identity of the cationic cluster

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Dedicated to Professor Dante Gatteschi on the occasion of his 60th birthday.

Abstract

The use of 2-pyridinealdoximate(−1) [(py)CHNO[−]] in nickel(II) chemistry has been further investigated. The synthetic investigation has led to two new salts of the very recently reported (in the form of its tetraperchlorate salt, **1**) enneanuclear cation [Ni₉(μ₃-OH)₂(μ₂-OH)₂{μ₃-(py)CHNO}₄{μ₂-(py)CHNO}₆(μ₂-OH)₂(H₂O)₆]⁴⁺. The two new cationic clusters [Ni₉(OH)₄{(py)CHNO}₁₀(H₂O)₈](SCN)₂(OH)₂ · 9.91H₂O (**2** · 9.91H₂O) and [Ni₉(OH)₄{(py)CHNO}₁₀(H₂O)₈]{N(CN)₂}₃(ClO₄) · 11.11H₂O (**3** · 11.11H₂O) have been structurally characterized by single-crystal X-ray crystallography at 100 K. The nature of the inorganic anions (Cl[−]/SCN[−], N(CN)₂[−]/ClO₄[−]) present in the reaction mixtures does not affect the chemical and structural identity of the enneanuclear cation. Characteristic IR data are discussed in terms of the nature of bonding and the structures of the complexes. The variable-temperature magnetic susceptibility data of **1**, which had also been obtained by our group, were simulated by means of a 3-*J* model, which is compared with the 2-*J* model reported for this cluster by Chaudhuri and co-workers [S. Khanra, T. Weyhermüller, E. Rentschler, P. Chaudhuri, *Inorg. Chem.* 44 (2005) 8176]. The ground-state total spin of the cluster is *S*_T = 1.

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1. Introduction

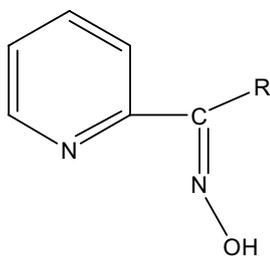
The last two decades have witnessed an explosive growth in the interest in polynuclear 3d-metal compounds (clusters) with oxygen- and/or nitrogen-based ligation [1]. This has been due to their relevance to two fields, bioinorganic chemistry and molecular magnetism. In the former

field, for example, some Fe and Mn clusters are of relevance to objectives such as understanding the formation of the multinuclear Fe/O core of ferritin [2], and investigating the nature and mechanism of action of the Mn₄Ca core of the water oxidizing complex in photosystem II [3]. In the latter area, the reason for the current intense interest in 3d-metal clusters is the often unusual and even novel magnetic properties that such species possess, e.g. single-molecule magnetism behaviour [4].

For the above and other fields/areas, there continues to be a great need for synthetic methods and reaction systems

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Scheme 1.

to new examples of homo- and heterometallic metal clusters to increase our knowledge of the structural, physical and spectroscopic properties of high nuclearity paramagnetic species. With this in mind, we have been exploring [5,6] the coordination chemistry of 2-pyridyl oximes [(py)C(R)NOH, Scheme 1], whose anions (py)C(R)NO[−] are versatile ligands for a variety of research objectives [7]. 2-pyridinealdoxime [IUPAC name: pyridine-2-carbaldehyde oxime, R = H in Scheme 1] occupies a special position amongst the 2-pyridyl oximes because: (i) it is the simplest 2-pyridyl oxime, (ii) its anion is a central player in the area of single-chain magnetism [8], and (iii) the in situ generated complex [Cu^{II}{(py)CHNO}₂(OH)][−] catalyses the selective oxidation of veratryl alcohol to aldehyde by O₂ in aqueous solution [9].

Our initial efforts with (py)CHNOH were concentrated on Mn [10] and Co [11] chemistry, and in late 2004 we decided to extend such reactions to Ni chemistry. The (py)CHNOH ligand has been used recently in homometallic Ni(II) cluster chemistry by Chaudhuri, who reported the remarkable triangular [Ni₃{(py)CHNO}₅{(py)CHNOH}] (ClO₄) complex [12], but we and his group [13] had suspected that there might be a number of other high nuclearity Ni_x^{II} species accessible. We have thus been studying the products from the reactions of (py)CHNOH with Ni(II) sources under a variety of conditions; irrespective of the inorganic anion(s) present and the “pH” value (within the 7–10 range) of the reaction system, the products of these reactions are all salts of the enneanuclear cation [Ni₉(μ₃-OH)₂(μ₂-OH)₂{μ₃-(py)CHNO}₄{μ₂-(py)CHNO}₆-(μ₂-OH)₂(H₂O)₆]⁴⁺. While our work had been at the stage of simulating the magnetic data and writing, Chaudhuri and co-workers communicated the perchlorate salt of this cation, i.e. complex [Ni₉(OH)₄{(py)CHNO}₁₀-(H₂O)₈](ClO₄)₄ · 12H₂O (**1** · 12H₂O) [13]. This cluster had been also characterized by our group¹ along with

other salts of the enneanuclear cation. Much to our regret, we have lost the opportunity to be the first to present this cationic cluster to the inorganic chemistry community! In this Note we report the preparation and single-crystal X-ray structures of two new salts of this cation, together with the magnetic characterization of one representative cluster of this family.

2. Experimental

All manipulations were performed under aerobic conditions using reagent grade materials (Aldrich, Alfa Aesar) and solvents as received. Complex **1** · 7.85H₂O · 1.4MeOH¹ was slowly crystallized from a NiCl₂ · 6H₂O/(py)CHNOH/NaClO₄ · H₂O (1:1:2) reaction mixture in H₂O–MeOH (3:1 v/v) at pH 8.1 (addition of aqueous 1 N NaOH). Typical yields were in the range 40–60%. The air-dried product was analyzed as **1** · 6H₂O.² IR spectra (4000–450 cm^{−1}) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. Magnetic susceptibility measurements in the range 2–300 K and magnetization measurements (2 K) in the field range −5 to 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. The data were corrected for diamagnetic contributions calculated from Pascal’s constants.

2.1. Compound preparation

2.1.1. [Ni₉(OH)₄{(py)CHNO}₁₀(H₂O)₈-(SCN)₂(OH)₂ · 9.91H₂O (**2** · 9.91H₂O)

2.1.1.1. Method A. To an orange solution of **1** · 6H₂O (0.364 g, 0.15 mmol) in MeCN (20 mL) was slowly added a solution of NaSCN (0.120 g, 1.48 mmol) in H₂O (8 mL) and solid NaOH (0.012 g, 0.30 mmol). The resulting yellow-green solution was kept under stirring for about 5 min and was allowed to slowly evaporate at room temperature. After several days brownish green crystals of the product formed, which were collected by filtration, washed with MeCN (2 mL) and Et₂O (2 × 3 mL), and dried in air. Yield: 40% (based on Ni^{II}). The air-dried solid was analyzed as **2** · 5H₂O. Anal. Calc. for C₆₂H₈₂Ni₉N₂₂S₂O₂₉: C, 33.97; H, 3.78; N, 14.06; S, 2.93. Found: C, 33.80; H, 3.84; N, 13.89; S, 3.00%. Main IR data (KBr pellet, cm^{−1}): 3411 sb, ~3200 sh, 2059 m, 1640 w, 1605 s, 1532 m, 1474 m, 1221 m, 1120 s, 1048 s, 776 m, 745 m, 684 m, 643 m, 526 m, 443 mb.

2.1.1.2. Method B. Solids NiCl₂ · 6H₂O (0.238 g, 1.00 mmol) and NaSCN (0.081 g, 1.00 mmol) were dissolved in H₂O (15 mL), resulting in a green solution. This was added to a colourless solution of (py)CHNOH (0.122 g, 1.00 mmol) in MeOH (5 mL) and the “pH” was adjusted to 8.0 using aqueous 1 N NaOH. The resulting

² Anal. Calc. for C₆₀H₈₂Ni₉N₂₀Cl₄O₄₄: C, 29.32; H, 3.37; N, 11.40. Found: C, 29.46; H, 3.22; N, 11.21%.

¹ Th.C. Stamatatos, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, P. Kyritsis, S.P. Perlepes, Proceedings of the 8th France–Italy–Greece–Israel–Portugal–Austria–Spain Meeting in Inorganic Chemistry, 6–9 July 2005, Athens, Greece, p. OP21. Our refinement led to the formula **1** · 7.85H₂O · 1.4MeOH. Crystal data: C_{61.40}H_{91.30}Ni₉N₂₀Cl₄O_{47.25}, formula weight 2535.83, monoclinic, C₂/c, a = 24.900(4) Å, b = 31.295(4) Å, c = 26.078(3) Å, β = 100.04(1)°, V = 2001.0(5) Å³, Z = 8, D_{calc} = 1.683 g cm^{−3}, T = 293(2) K, μ (Cu Kα) = 3.646 mm^{−1}, 14458 reflections collected, 14098 unique (R_{int} = 0.0298), 1468 refined parameters, 11864 observed reflections [I > 2σ(I)], R₁ = 0.0777 [I > 2σ(I)], wR₂ = 0.2050 [I > 2σ(I)].

new olive green solution was stirred for about 1 h, filtered and allowed to slowly concentrate at room temperature. After 4–5 days brownish green crystals of the product were precipitated. The crystals were collected by filtration, washed with ice-cold MeOH (1 mL) and Et₂O (2 mL), and dried in air. Yield: ~70% (based on the ligand). The dried solid was analyzed satisfactorily as **2** · 5H₂O. The identity of the product was further confirmed by IR spectroscopic comparison with the authentic sample prepared by method A.

2.1.2. [Ni₉(OH)₄{(py)CHNO}₁₀(H₂O)₈]{N(CN)₂}₃ · (ClO₄)₄ · 11.11H₂O (**3** · 11.11H₂O)

Solids Ni(ClO₄)₂ · 6H₂O (0.183 g, 0.50 mmol), (py)CHNOH (0.061 g, 0.50 mmol) and NaN(CN)₂ (0.089 g, 1.00 mmol) were dissolved in H₂O (20 mL), resulting in a green solution. The pH of the reaction solution was adjusted to 6.5 using aqueous 1 N NaOH and the obtained slurry was dissolved upon addition of MeCN (10 mL) under vigorous stirring. The resulting homogenous, olive green solution was further stirred for 30 min and allowed to slowly concentrate at room temperature. The evaporation gave X-ray quality, brownish green crystals of the product. The crystals were collected by filtration, washed with cold MeCN (1 mL) and Et₂O (2 mL), and dried in air. Yield: 65% (based on the ligand). The air-dried solid was analyzed as **3** · 10H₂O. Anal. Calc. for C₆₆H₉₀Ni₉N₂₉ClO₃₆: C, 32.63; H, 3.74; N, 16.72. Found: C, 32.80; H, 3.69; N, 16.60%. Main IR data (KBr pellet, cm⁻¹): ~3400 sb, 3220 mb, 2277 m, 2236 s, 2188 m, 1603 s, 1533 m, 1474 m, 1228 m, 1128 s, 1091 s, 1046 s, 775 m, 682 m, 642 s, 628 w, 525 m, 445 mb.

2.2. Single-crystal X-ray crystallography

Crystals of **2** · 9.91H₂O and **3** · 11.11H₂O were mounted in Paratone-N oil. Diffraction measurements were made on an Oxford Diffraction CCD instrument using graphite-monochromated Mo radiation. Complete crystal data and parameters for data collection and processing are reported in Table 1. Unit cell dimensions were determined and refined by using 33 689 (4.0 ≤ θ ≤ 29.3°) and 14 045 (3.0 ≤ θ ≤ 31.2°) reflections for **2** · 9.91H₂O and **3** · 11.11H₂O, respectively. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software [14].

The structures were solved by direct methods using SIR-92 [15a] and refined by full-matrix least-squares techniques on F² using SHELXL-97 [15b]. The programs used were CrysAlis CCD [14] for data collection, CrysAlis RED [14] for cell refinement and data reduction, and ORTEP-3 [16a], PLATON [16b] and MERCURY [16c] for molecular graphics. All non-hydrogen atoms of the two structures were refined anisotropically. Both structures contain a few highly disordered H₂O molecules making it thus difficult to model their positions and distribution reli-

Table 1
Crystallographic data for complexes **2** · 9.91H₂O and **3** · 11.11H₂O

Parameter	2 · 9.91H ₂ O	3 · 11.11H ₂ O
Formula	C ₆₂ H _{91.81} Ni ₉ N ₂₂ · S ₂ O _{33.91}	C ₆₆ H _{92.21} Ni ₉ N ₂₉ · ClO _{37.11}
Formula weight	2280.33	2449.46
Crystal system	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	18.229(1)	15.228(1)
<i>b</i> (Å)	18.283(1)	16.799(1)
<i>c</i> (Å)	19.797(1)	22.326(1)
α (°)	71.15(1)	106.76(1)
β (°)	74.26(1)	98.03(1)
γ (°)	64.52(1)	96.18(1)
<i>V</i> (Å ³)	5569.0(6)	5348.6(6)
<i>Z</i>	2	2
<i>D</i> _{calc} (Mg m ⁻³)	1.360	1.521
μ (Mo K α) (mm ⁻¹)	1.597	1.660
Temperature (K)	100(2)	100(2)
$2\theta_{\max}$ (°)	49.0	53.0
Reflections collected	63 693	62 223
Unique reflections (<i>R</i> _{int})	16 562 (0.042)	20 025 (0.069)
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	12 901	11 746
Parameters refined	1173	1291
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	2.269, -0.938	1.933, -0.791
Goodness-of-fit on <i>F</i> ²	1.089	1.008
Final <i>R</i> ₁ ^a and <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0985 and 0.2690	0.0712 and 0.1695

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$$

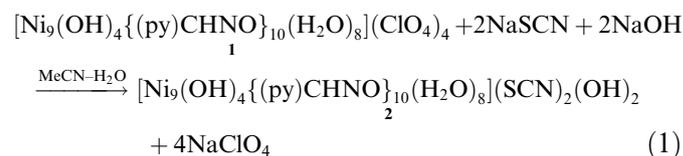
$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

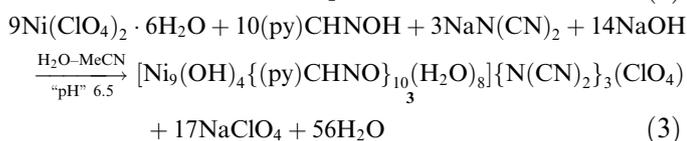
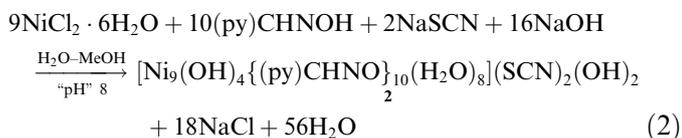
ably. Therefore, the SQUEEZE strategy of PLATON [17] was used to remove the disordered solvent contribution from the intensity data, leading to an improved model and a significant drop of the *R*₁ values. One solvate H₂O molecule of **2** · 9.91H₂O and three H₂O molecules of **3** · 11.11H₂O were refined with partial occupation factors; in addition, one disordered H₂O molecule of **2** · 9.91H₂O was modelled on two sites with occupancies adding up to 1. Restraints were employed in the refinement to keep similar the geometry and the anisotropic displacement parameters of the SCN⁻ and N(CN)₂⁻ counterions of **2** · 9.91H₂O and **3** · 11.11H₂O, respectively. The hydrogen atoms attached to carbon atoms of the (py)CHNOH ligands were positioned geometrically (riding model). No hydrogen atoms for the aqua ligands and solvate molecules were included in the refinement.

3. Results and discussion

3.1. Brief synthetic comments and IR spectra

The preparation of **2** (by both methods) and **3** can be summarized in balanced Eqs. (1)–(3).





Some features of the reactions represented by Eqs. (1)–(3) deserve brief comments. First, the metathesis reaction that leads to **2** [Eq. (1)] needs to be carried out in a solvent mixture containing H_2O to ensure non-contamination of the solid product with NaClO_4 . Second, despite the coordinating ability of SCN^- and $\text{N}(\text{CN})_2^-$, these anions appear only as counterions in **2** and **3**; this fact is a strong evidence for the great thermodynamic stability of $[\text{Ni}_9(\text{OH})_4\{(\text{py})\text{CHNO}\}_{10}(\text{H}_2\text{O})_8]^{4+}$. Third, the large excess of SCN^- and $\text{N}(\text{CN})_2^-$ in the reaction mixtures does not lead to cationic complexes containing four such counteranions; presumably, the presence of OH^- and ClO_4^- counteranions in **2** and **3**, respectively, satisfies lattice requirements. The presence of OH^- counterions has precedent in cluster chemistry [18]. And fourth, increase of the “pH” of the reaction systems up to 10 does not affect the identity of the products (analytical and IR evidence).

The IR spectra of dried samples of **2** and **3** exhibit two medium to strong intensity bands in the 3450–3200 cm^{-1} region, assignable to $\nu(\text{OH})_{\text{OH}^-/\text{H}_2\text{O}}$. Two bands, one strong at 1605–1603 and two strong at ~ 1125 and ~ 1045 cm^{-1} are assigned [11,12] to the oximate $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{O})$ modes, respectively. The appearance of two sharp NO stretching vibrations (~ 1125 , ~ 1045 cm^{-1}) is consistent with the presence of two different coordination modes of the oximate group in **2** and **3** (vide infra) [12]. Complex **2** exhibits the $\nu(\text{CN})$ and $\nu(\text{CS})$ modes of SCN^- at 2059 and 745 cm^{-1} , respectively; these wavenumbers are very close to those of the corresponding bands of KSCN (2053, 748 cm^{-1}), in agreement with the ionic character of the thiocyanates in **2** [19]. The IR spectrum of **3** exhibits bands at 1091 and 628 cm^{-1} , due to the $\nu_3(F_2)$ [$\nu_d(\text{ClO})$] and $\nu_4(F_2)$ [$\delta_d(\text{OCIO})$] modes, respectively, of the uncoordinated T_d ClO_4^- [19]. The dicyanamide free anion in $\text{NaN}(\text{CN})_2$ shows three sharp and medium to strong characteristic stretching bands in the 2290–2170 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}), $\nu_{\text{as}}(\text{C}=\text{N})$ [2232 cm^{-1}] and $\nu_{\text{s}}(\text{C}=\text{N})$ [2179 cm^{-1}] [20]. These vibrations appear in **3** almost at the same wavenumbers (2277, 2236 and 2188 cm^{-1}) as the corresponding ones in $\text{NaN}(\text{CN})_2$, spectroscopically confirming the ionic nature of the dicyanamides in **3** [20].

3.2. Description of structures

The molecular structures of the enneanuclear cations present in complexes **2** · 9.91 H_2O and **3** · 11.11 H_2O are

almost identical. Thus, only the structure of the latter (as a representative example) will be discussed. A partially labelled plot of the cation of **3** · 11.11 H_2O is shown in Fig. 1; its core is illustrated in Fig. 2. Selected interatomic distances and angles are listed in Table 2.

The structure of **3** · 11.11 H_2O consists of the enneanuclear cation $[\text{Ni}_9(\text{OH})_4\{(\text{py})\text{CHNO}\}_{10}(\text{H}_2\text{O})_8]^{4+}$, $\text{N}(\text{CN})_2^-$ and ClO_4^- counterions, and solvate H_2O molecules; the counteranions and solvate molecules will not be further discussed. The enneanuclear cationic assembly is held together by two μ_3 - OH^- ligands [O(13), O(16)], two μ_2 - OH^- ligands [O(11), O(15)], two μ_2 -aqua ligands [O(12), O(14)], six μ_2 -oximate groups [N(2)–O(1), N(4)–O(2), N(10)–O(5), N(12)–O(6), N(16)–O(8), N(20)–O(10)] and four μ_3 -oximate groups [N(6)–O(3), N(8)–O(4), N(14)–O(7), N(18)–O(9)]; peripheral ligation is provided by the ten 2-pyridyl nitrogen atoms [N(1), N(3), N(5), N(7), N(9), N(11), N(13), N(15), N(17), N(19)] and six terminal aqua ligands [O(17)–O(22)]. Thus, the core appears to be $\{\text{Ni}_9(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2(\mu_3\text{-ONR})_4(\mu_2\text{-ONR})_6(\mu_2\text{-OH}_2)_2\}$. Atom Ni(1) can be regarded as a pseudo-inversion center. The cation can be conveniently described as consisting of two $[\text{Ni}_4(\mu_2\text{-OH})_2\{\mu_2\text{-}(\text{py})\text{CHNO}\}_5(\mu_2\text{-OH}_2)(\text{H}_2\text{O})_3]^{2+}$ subunits linked to the central Ni(1) ion through four oximate oxygens [O(3), O(4), O(7), O(9)] and two *trans* disposed bridging OH^- groups; as a result of this connection, one OH^- ligand of each subunit [O(13), O(16)] becomes μ_3 , and two oximate oxygens of each subunit [O(3), O(4), O(7), O(9)] become μ_2 giving an overall μ_3 character in the corresponding (py)CHNO $^-$ ligands. As a result of the above described ligation the distorted octahedral chromophores are Ni(1)($\text{O}_{\text{oximate}}$) $_4(\text{O}_{\mu_3\text{-hydroxo}})_2$, Ni(2, 6)($\text{O}_{\text{oximate}}$) $_2(\text{O}_{\mu_2\text{-hydroxo}})(\text{O}_{\text{aqua}})\text{N}_2$, Ni(3, 5)($\text{O}_{\mu_2\text{-hydroxo}})(\text{O}_{\mu_2\text{-aquo}})\text{N}_4$, Ni(4, 8)($\text{O}_{\text{oximate}}$) $_2(\text{O}_{\mu_3\text{-hydroxo}})(\text{O}_{\mu_2\text{-aquo}})\text{N}_2$ and Ni(7, 9)($\text{O}_{\text{oximate}}$) $_2(\text{O}_{\mu_3\text{-hydroxo}})(\text{O}_{\text{aquo}})_2\text{N}_2$.

Six of the (py)CHNO $^-$ ions function as $\eta^1:\eta^1:\eta^1:\mu_2$ ligands (or as 2.1 $_1$ 1 $_2$ 1 $_2$ ligands using Harris notation [21]), whereas the remaining four behave as $\eta^1:\eta^1:\eta^2:\mu_3$ (3.2 $_1$, 2 $_1$ 1 $_3$ 1 $_3$ [21]) ligands, see Scheme 2.

The Ni– $\text{O}_{\mu_3\text{-hydroxo}}$, Ni– $\text{O}_{\mu_2\text{-hydroxo}}$, Ni– $\text{O}_{\mu_2\text{-aquo}}$, Ni– O_{aquo} , Ni– $\text{O}_{\mu_2\text{-oximate}}$, Ni– $\text{O}_{\text{oximate}}$, Ni– $\text{N}_{\text{pyridyl}}$ and Ni– $\text{N}_{\text{oximate}}$ bond lengths are in the ranges 1.989(5)–2.037(4), 2.002(5)–2.015(5), 2.141(5)–2.162(4), 2.069(5)–2.126(4), 2.117(5)–2.198(5), 2.036(5)–2.073(5), 2.045(6)–2.093(6) and 2.006(6)–2.066(6) Å, respectively. All bond lengths are typical for high-spin, six-coordinate Ni(II) complexes [12,13,20]. The Ni–O bonds to the bridging hydroxo ligands [average values: 2.010(5) and 2.011(5) Å for μ_3 - and μ_2 - OH^- s, respectively] are shorter, as expected, than those to the bridging aqua ligands [average value: 2.147(5) Å]. The bridging aqua ligands form slightly weaker bonds to the metal ions [average value: 2.147(5) Å] than the terminal aqua ligands [average value: 2.099(5) Å]. The Ni–O bond distances for the bridging oximate oxygen atoms [average value: 2.140(5) Å] are longer than the Ni–O distances exhibited by the terminal oximate oxygen atoms [average value: 2.054(5) Å], as expected. The

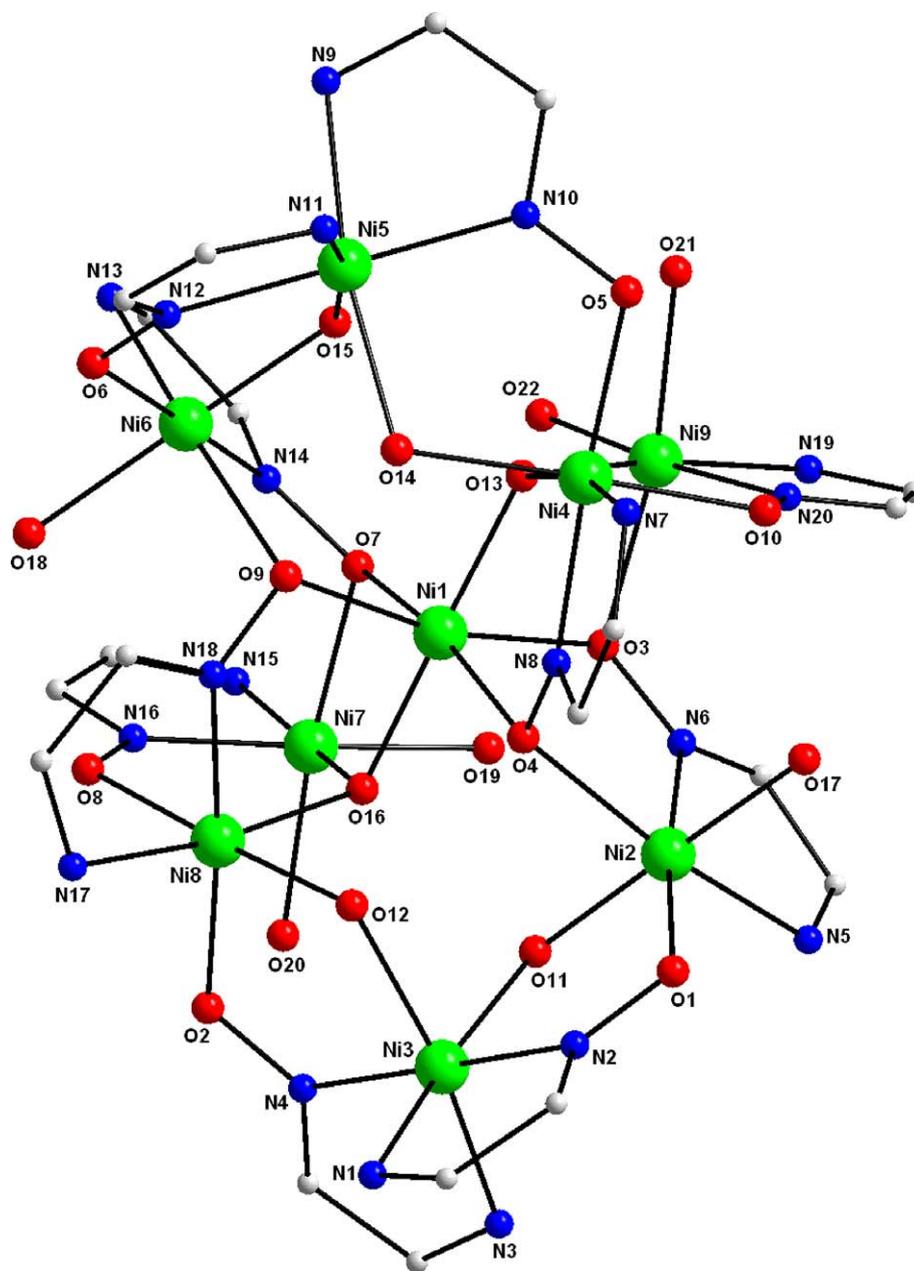


Fig. 1. A view of the cation of complex $3 \cdot 11.11\text{H}_2\text{O}$. To avoid congestion, most carbon atoms of the ten $(\text{py})\text{CHNO}^-$ ligands have been omitted. Atoms O(1)–O(10) belong to the deprotonated 2-pyridinealdoximate ligand. Atoms O(13) and O(16) belong to the $\mu_3\text{-OH}^-$ ligands, while atoms O(11) and O(15) belong to the $\mu_2\text{-OH}^-$ ligands; the $\mu_2\text{-H}_2\text{O}$ oxygen atoms are O(12) and O(14), while O(17)–O(22) are the oxygen atoms of the terminal H_2O ligands.

nine Ni^{II} ions do not seem to define any established topology. The supramolecular structure of the complex is built up by a variety of $\text{O-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{N}_{\text{dicyanamide}}$ hydrogen bonds, as deduced from the $\text{O}\cdots\text{O}$ and $\text{O}\cdots\text{N}$ distances.

The molecular structures of the cations $[\text{Ni}_9(\text{OH})_4\{(\text{py})\text{CHNO}\}_{10}(\text{H}_2\text{O})_8]^{4+}$ of complexes $2 \cdot 9.91\text{H}_2\text{O}$ and $3 \cdot 11.11\text{H}_2\text{O}$ are almost identical to the structure of the cation present in the perchlorate salt $1 \cdot 12\text{H}_2\text{O}$ [13].¹ Complexes 2 and 3 join a very small family of structurally characterized, non-organometallic enneanuclear $\text{Ni}(\text{II})$ clusters possessing N- and/or O-ligands [13,23].¹ These compounds are also extremely rare examples of 2-pyridinealdoxi-

mate(−1) metal complexes with two different coordination modes of the anionic ligand, the previously reported examples being clusters $[\text{Ni}_3\{(\text{py})\text{CHNO}\}_5\{(\text{py})\text{CHNOH}\}] \cdot (\text{ClO}_4)$ [12] and $[\text{Mn}_6\{(\text{py})\text{CHNO}\}_8\{(\text{py})\text{CHNOH}\}_4] \cdot (\text{ClO}_4)_4$ [23].

3.3. Magnetic properties

Solid state dc magnetic susceptibility studies were performed for analytically pure samples of complexes 1–3 in the range of 2–300 K under a field of 0.1 T. The three complexes exhibit a very similar magnetic behaviour. We shall briefly discuss here the magnetic properties only for

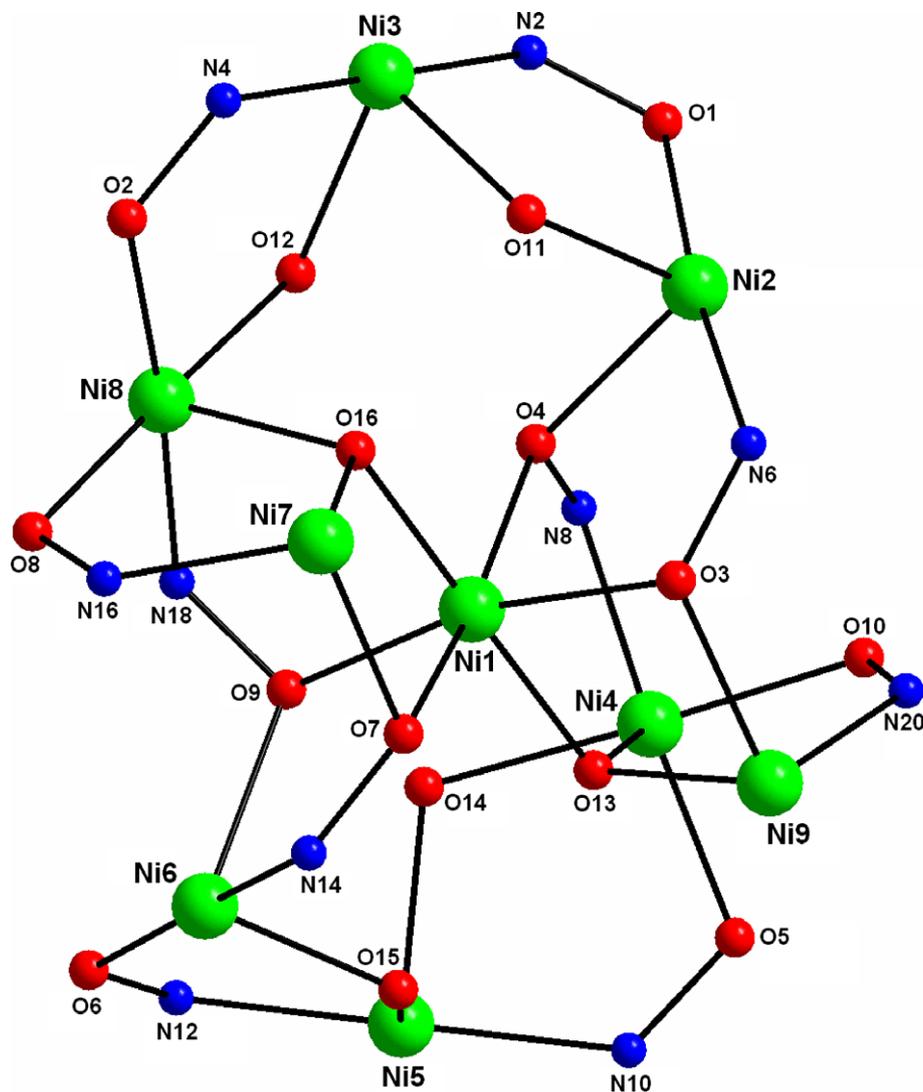


Fig. 2. The $\{\text{Ni}_9(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2(\mu_3\text{-ONR})_4(\mu_2\text{-ONR})_6(\mu_2\text{-OH}_2)_2\}$ core of complex **3** · 11.11H₂O, where R = (py)CH. For the chemical nature of the oxygen atoms, see the caption of Fig. 1. The shown nitrogen atoms belong to the oximate groups.

the representative perchlorate salt **1** reported by Chaudhuri's group [13], and also prepared and characterized by our group.^{1,2} The reason for the selection of **1** is the fact that we have carried out a different magnetic analysis compared to the treatment by Chaudhuri and co-workers [13] and thus a comparison of the two models can be made.

The $\chi_{\text{M}}T$ versus T plot for **1** · 6H₂O^{1,2} is shown in Fig. 3. The room-temperature value of $\chi_{\text{M}}T$ (8.40 cm³ mol⁻¹ K) is lower than the spin-only value expected for nine isolated Ni^{II} atoms (9.0 cm³ mol⁻¹ K with $g_{\text{Ni}} = 2.00$), indicative of antiferromagnetic coupling, even at 300 K. The product decreases continuously with decreasing temperature, reaching a value of 1.00 cm³ mol⁻¹ K at 2 K. Magnetization experiments up to a field of 5 T show a saturation value equivalent to two electrons, indicating an $S_{\text{T}} = 1$ ground state.

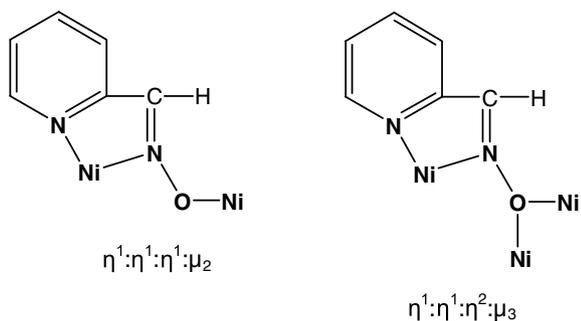
Complex **1** has no crystallographic symmetry; therefore, in principle, there are a large number (totally 16) of inde-

pendent exchange interactions through the μ_2 - and μ_3 -oximate groups, the μ_2 - and μ_3 -OH⁻ groups, and the aqua bridges (μ_2 -H₂O). To avoid a vast overparametrization, we decided to attempt to fit the susceptibility data using the simple 3- J model shown graphically in Fig. 4. Since the μ_2 -aqua ligands are poor superexchange mediators [13,24], we have neglected this pathway [13]. Various details of the coupling scheme are also given in the caption of Fig. 4. Best-fit parameters obtained by means of the program CLUMAG, which uses the irreducible tensor operator (ITO) formalism [25], are $J_1 = -16.4$ cm⁻¹, $J_2 = -8.7$ cm⁻¹, $J_3 = -27.1$ cm⁻¹ and $g = 2.079$ ($R = 1.1 \times 10^{-3}$). Analysis of the spin energy levels indicates an $S_{\text{T}} = 1$ ground state, in good agreement with the magnetization experiments.

The obtained J values are in satisfactory agreement with magnetostructural trends found in Ni(II) oximate cluster chemistry. All oximate-bridged Ni(II) complexes, that have

Table 2
Selected interatomic distances (Å) and bond angles (°) for complex $3 \cdot 11.11\text{H}_2\text{O}$

Ni(1)···Ni(9)	3.099(1)	Ni(5)–O(15)	2.011(5)
Ni(3)···Ni(5)	8.904(1)	Ni(5)–N(12)	2.025(7)
Ni(1)–O(3)	2.125(5)	Ni(6)–O(9)	2.198(5)
Ni(1)–O(13)	2.004(4)	Ni(6)–O(15)	2.015(5)
Ni(2)–O(1)	2.043(5)	Ni(6)–O(18)	2.095(5)
Ni(2)–O(11)	2.002(5)	Ni(7)–O(16)	2.015(5)
Ni(2)–N(5)	2.079(6)	Ni(7)–O(20)	2.123(5)
Ni(3)–O(11)	2.015(5)	Ni(7)–N(15)	2.063(6)
Ni(3)–O(12)	2.162(4)	Ni(8)–O(2)	2.036(5)
Ni(3)–N(4)	2.017(6)	Ni(8)–O(12)	2.142(4)
Ni(4)–O(5)	2.073(5)	Ni(8)–O(16)	2.019(5)
Ni(4)–O(13)	2.037(4)	Ni(9)–O(13)	1.989(5)
Ni(4)–O(14)	2.141(5)	Ni(9)–O(22)	2.069(5)
Ni(5)–O(14)	2.141(5)	Ni(9)–N(19)	2.045(6)
O(3)–Ni(1)–O(9)	166.8(2)	N(10)–Ni(5)–N(12)	176.7(3)
O(4)–Ni(1)–O(7)	167.3(2)	O(6)–Ni(6)–N(14)	175.0(2)
O(13)–Ni(1)–O(16)	177.7(2)	O(9)–Ni(6)–N(13)	165.8(2)
O(1)–Ni(2)–N(6)	174.0(2)	O(15)–Ni(6)–O(18)	174.3(2)
O(4)–Ni(2)–N(5)	167.0(2)	O(7)–Ni(7)–O(20)	170.1(2)
O(11)–Ni(2)–O(17)	175.7(2)	O(16)–Ni(7)–N(15)	169.4(2)
O(11)–Ni(3)–N(1)	168.0(2)	O(19)–Ni(7)–N(16)	173.5(2)
O(12)–Ni(3)–N(3)	168.9(2)	O(2)–Ni(8)–N(18)	175.1(2)
N(2)–Ni(3)–N(4)	176.1(3)	O(8)–Ni(8)–O(12)	176.8(2)
O(5)–Ni(4)–N(8)	175.8(2)	O(16)–Ni(8)–N(17)	170.7(2)
O(10)–Ni(4)–O(14)	177.7(2)	O(3)–Ni(9)–O(21)	170.2(2)
O(13)–Ni(4)–N(7)	167.7(2)	O(13)–Ni(9)–N(19)	169.4(2)
O(14)–Ni(5)–N(9)	170.3(3)	O(22)–Ni(9)–N(20)	172.2(2)
O(15)–Ni(5)–N(11)	168.6(2)		



magnetically been characterized [5,7,12,13], exhibit weak to moderate antiferromagnetic interactions. That the J_1 and J_3 interactions are the strongest ones is consistent with the fact that these are partially (J_1) or exclusively (J_3) mediated by a diatomic oximate $=\text{N}-\text{O}^-$ bridge ($\eta^1:\eta^1:\mu_2$ oximate group) [12,13], which is expected to provide the main superexchange σ -pathway. Taking into account that the Ni–O–Ni bond angles related to J_2 are in the 93.6–102.8° range, the weaker antiferromagnetic value of this coupling constant is understandable [26]. It should be stressed at this point that the magnetic susceptibility data of **1** were recently successfully simulated by Chaudhuri and co-workers who employed a simpler 2- J model [13]. The best-fit parameters were $J = -26.5 \text{ cm}^{-1}$, $J' = -7.0 \text{ cm}^{-1}$, with $g = 2.15$, where J represents the interaction through

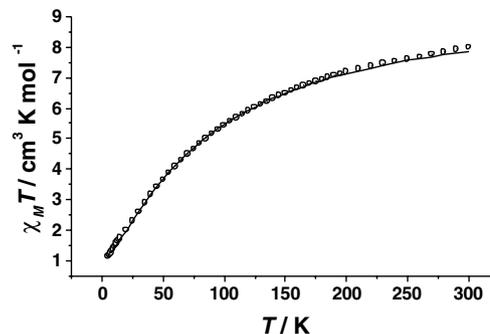


Fig. 3. Plot of the $\chi_M T$ product vs. T for a polycrystalline sample of complex $1 \cdot 6\text{H}_2\text{O}$.² The solid line is the fit of the experimental data to the appropriate 3- J model; see the text for the fitting parameters.

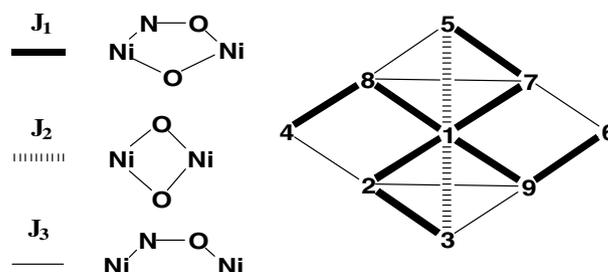


Fig. 4. The 3- J magnetic model used for complex **1**. The single O atom that contributes to the coupling constant J_1 belongs to a $\mu_3\text{-OH}^-$, a $\mu_2\text{-OH}^-$ or to a μ_3 -oximate group. One of the O atoms that create the J_2 constant is a μ_2 -oximate oxygen (belonging to a μ_3 -oximate group), whereas the second O atom belongs to a $\mu_3\text{-OH}^-$ group. The numbering scheme used for the Ni^{II} atoms is the same with that used in the solution of the structure of $1 \cdot 7.85\text{H}_2\text{O} \cdot 1.4\text{MeOH}^{\text{I}}$ (not described in this paper for reasons outlined in Section 1). Atoms Ni(1), Ni(2), Ni(3), Ni(4), Ni(5), Ni(6), Ni(7), Ni(8) and Ni(9) of the shown interaction scheme correspond to atoms Ni(1), Ni(8), Ni(7), Ni(3), Ni(9), Ni(5), Ni(4), Ni(2) and Ni(6), respectively, of the structure of $3 \cdot 11.11\text{H}_2\text{O}$ (Figs. 1 and 2) described in this Note.

$\mu_2 = \text{N}-\text{O}^-$ and $\mu_2\text{-OH}^-$ groups, whereas J' represents the paths involving μ_3 -oximate, $\mu_2 = \text{N}-\text{O}^-$ and $\mu_3\text{-OH}^-$ groups.

4. Concluding comments and perspectives

The present work extends the body of results that emphasize the ability of the monoanionic ligand (py)CHNO⁻ to form interesting structural types in 3d-metal chemistry. The use of 2-pyridinealdoxime in reactions with Ni(II) sources has provided access to new salts of the thermodynamically stable enneanuclear cation $[\text{Ni}_9(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2\{\mu_3\text{-(py)CHNO}\}_4\{\mu_2\text{-(py)CHNO}\}_6\text{-(}\mu_2\text{-OH}_2)_2(\text{H}_2\text{O})_6]^{4+}$. The nature of the inorganic anions present in the reaction systems (Cl^-/SCN^- , $\text{N}(\text{CN})_2^-/\text{ClO}_4^-$) has no effect on the identity of the complex cation. The clusters have an $S_T = 1$ ground state and their magnetic behaviour can successfully be modeled using a realistic 3- J model. The terminal aqua ligands present in **1–3** could have future utility as sites for facile incorporation

of other neutral or anionic monodentate ligands by metathesis reactions or as a means of accessing higher-nuclearity species by using bis(monodentate) bridging aromatic heterocycles. Since the intended bridging behaviour of SCN^- and $\text{N}(\text{CN})_2^-$ has not been achieved in **2** and **3**, we are intensively pursuing our efforts to substitute the hydroxo bridges by end-on azido bridging ligands according to our well-developed general synthetic strategy [22h,27]. Work in progress at the time of writing also reveals that replacement of (py)CHNOH by (py)C(Me)NOH ($\text{R} = \text{CH}_3$, Scheme 1) or (py)C(ph)NOH ($\text{R} = \text{C}_6\text{H}_5$, Scheme 1) in otherwise analogous reaction systems has a dramatic effect on the structural and magnetic identity of the obtained nickel(II) clusters.

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Appendix A. Supplementary data

Crystallographic data for complexes $2 \cdot 9.91\text{H}_2\text{O}$ and $3 \cdot 11.11\text{H}_2\text{O}$ (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 602257 and 602391, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.04.021.

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