

Research Article

Synthesis and Structural Characterization of a New Tetranuclear Nickel(II) Sulfato Complex Containing the Anionic Form of Di-2-Pyridyl Ketone Oxime

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The preparation and crystal structure of a tetranuclear Ni(II) sulfato cluster containing the anion of di-2-pyridyl ketone oxime, $(\text{py})_2\text{CNO}^-$, are reported. Treatment of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ with one equivalent of $(\text{py})_2\text{CNOH}$ and one equivalent of NEt_3 in MeOH leads to the compound $[\text{Ni}_4\{(\text{py})_2\text{CNO}\}_4(\text{SO}_4)_2(\text{MeOH})_4]$ (**1**) in moderate yield. The metal ions are linked together by two 3.2111 and two 2.1110 (Harris notation) $(\text{py})_2\text{CNO}^-$ ligands, as well as two 2.1100 SO_4^{2-} ions to create a rare metallocrown-type (12-MC-4) ring. Strong H-bond intermolecular interactions in **1** lead to the formation of a 1D chain along the *c* axis. Characteristic IR bands are discussed in terms of the known structure of **1**.

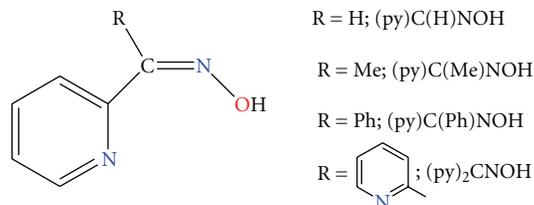
1. Introduction

There is currently a renewed interest in the coordination chemistry of oximes [1–20]. 2-pyridyl oximes (Scheme 1) are popular ligands in coordination chemistry [21–36]. The anions of these molecules are versatile ligands for a variety of research objectives, including μ_2 and μ_3 behaviour [21, 22]; the activation of 2-pyridyl oximes by 3d-metal centers towards further reactions is also becoming a fruitful area of research [21, 22, 26]. The majority of the metal complexes of these ligands have been prepared in the last 15 years and much of their chemistry remains to be explored in more detail [22].

We have been exploring “ligand blend” reactions involving carboxylates ($\text{R}'\text{CO}_2^-$) and various 2-pyridyloximates with (ternary “ligand blends”) or without (binary “ligand blends”) additional inorganic monoanions (Cl^- , Br^- , NO_3^- , N_3^- , SCN^-) as a means to high-nuclearity species. The presence of a deprotonated oxime group leads to a great coordinative flexibility due to the well-known ability of the oximate group to bridge two or three metal ions. On the other hand, carboxylates are able to deprotonate the oxime

group of 2-pyridyloximes under mild conditions (the use of external hydroxides often perplexes the reactions). Besides their deprotonating ability, the $\text{R}'\text{CO}_2^-$ ions are flexible ligands, a consequence of their ability to adopt a number of different ligation modes, both terminal and bridging as well as both bidentate and tridentate. The additional inorganic monoanions in the ternary “ligand blends” often behave as terminal ligands and help the formation of clusters (and not coordination polymers). However, sometimes they act as bridging ligands, and this may eventually lead to clusters with complicated structures; the formation of coordination polymers cannot be ruled out in such a case. Thus, a variety of Cr, Mn, Fe, Co, Ni, and Cu clusters [22–39] with nuclearities ranging from 3 to 12 have been characterized from our [23–36] and other [21, 37–39] groups, some of them possessing interesting magnetic properties, including single-molecule magnetism behaviour [33, 40].

Recently, we have begun a program which can be considered as a modification of the above-mentioned binary “ligand blend” approach. We have been exploring the use of other inorganic ions, such as SO_4^{2-} , instead of the carboxylate ligand, $\text{R}'\text{CO}_2^-$, in the 3d-metal cluster



SCHEME 1: General structural formula and abbreviations of simple 2-pyridyl oximes.

chemistry with 2-pyridyloximate ligands. The sulfate ion [41] is a ligand with great coordinative flexibility (μ_2 , μ_3 , μ_4 , μ_5 , μ_6 , μ_8 , or μ_{10} potential), see Scheme 2. Metal-sulfato complexes have been studied for their roles in the field of porous framework materials [42, 43], in catalysis [44], in the construction of luminescent molecular materials [45, 46], and in medicinal [47], environmental [48], and bioinorganic [49] chemistry. The possible advantages of using SO_4^{2-} instead of $\text{R}'\text{CO}_2^-$ include (i) the possibility of triggering aggregation of preformed smaller cationic species 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. Thus, the initial employment of the sulfate ion in $\text{Ni}^{\text{II}}/(\text{py})\text{C}(\text{R})\text{NOH}$ (R = Me, Ph, NH_2) chemistry has led to the isolation and characterization of high-nuclearity Ni^{II} compounds, such as Ni_{12} [50] and Ni_6 [51, 52] clusters which possess interesting structural properties.

In this work, we expand our efforts to a different member of 2-pyridyl oximes which is di-2-pyridyl ketone oxime, $(\text{py})_2\text{CNOH}$, and report the synthesis and characterization of the new tetranuclear compound $[\text{Ni}_4\{(\text{py})_2\text{CNO}\}_4(\text{SO}_4)_2(\text{MeOH})_4]$. The structure of the compound has been determined by single-crystal X-ray diffraction. The IR data are discussed in terms of the nature of bonding and the structure of the complex.

2. Experimental

2.1. General and Physical Measurements. All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets.

2.2. Compound Preparation

2.2.1. $[\text{Ni}_4\{(\text{py})_2\text{CNO}\}_4(\text{SO}_4)_2(\text{MeOH})_4]$ (1**).** NEt_3 (0.139 ml, 1.00 mmol) was added to a colourless solution of $(\text{py})_2\text{CNOH}$ (0.199 g, 1.00 mmol) in MeOH (25 ml). Subsequently, solid $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.263 g, 1.00 mmol) was added, and the resulting red solution was stirred for 1 h at room temperature. A small quantity of undissolved material was

TABLE 1: Summary of crystal data, data collection, and structure refinement for the X-ray diffraction study of complex **1**.

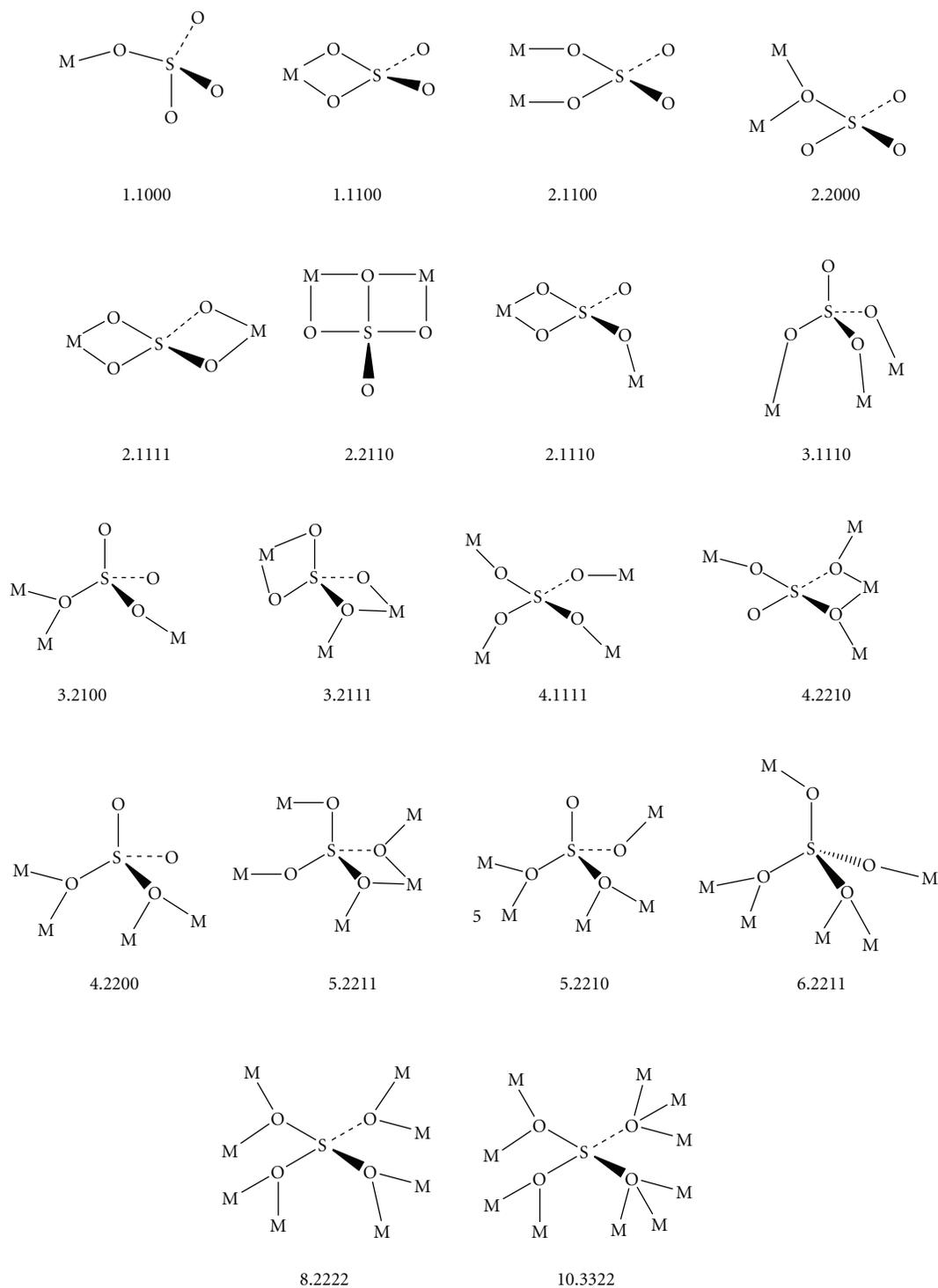
Complex	1
Empirical formula	$\text{Ni}_4\text{C}_{48}\text{H}_{48}\text{N}_{24}\text{O}_{16}\text{S}_2$
Formula weight	1515.97
Colour, habit	orange, rod
Crystal system	orthorhombic
Space group	P_{ccn}
a (Å)	14.2969 (10)
b (Å)	20.9678 (14)
c (Å)	18.5395 (13)
V (Å ³)	5557.7 (7)
Z	4
ρ_{calc} (g cm ⁻³)	1.609
Radiation, λ (Å)	0.71073
μ (mm ⁻¹)	1.488
$F(000)$	2760
Temperature (K)	100 (2)
$2\theta_{\text{max}}$ [°]	61
Ranges h	-18 - 18
k	-21 - 27
l	-27 - 23
Measured reflections	42848
Unique reflections	6377
Reflections used	3703
($I > 2\sigma(I)$)	
Parameters refined	374
GoF (on F^2)	0.903
R_1^a ($I > 2\sigma(I)$)	0.0464
wR_2^b ($I > 2\sigma(I)$)	0.1042
$(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}}$ (e Å ⁻³)	0.861/-0.621

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

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

removed by filtration and the dark red filtrate layered with Et_2O (50 ml). Slow mixing gave X-ray quality, orange crystals which were collected by filtration, washed with Et_2O (2×3 ml), and dried in air; yield 57%. The dried solid was analyzed satisfactorily as $\mathbf{1} \cdot \text{MeOH}$. Anal. Calc. for $\text{C}_{49}\text{H}_{52}\text{Ni}_4\text{N}_{24}\text{O}_{17}\text{S}_2$: C, 38.02; H, 3.99; N, 21.72. Found: C, 38.45; H, 3.87; N, 21.37%. IR (KBr pellet): $\tilde{\nu} = 3388\text{ s, } 2902\text{ w, } 1654\text{ w, } 1598\text{ m, } 1460\text{ m, } 1430\text{ m, } 1376\text{ w, } 1340\text{ w, } 1282\text{ w, } 1219\text{ m, } 1130\text{ m, } 1118\text{ s, } 1086\text{ s, } 1045\text{ s, } 1020\text{ m, } 982\text{ m, } 896\text{ w, } 788\text{ w, } 748\text{ m, } 702\text{ m, } 670\text{ m, } 641\text{ m, } 618\text{ s, } 591\text{ w, } 452\text{ w cm}^{-1}$.

2.3. Single-Crystal X-Ray Crystallography. A crystal of **1** with appropriate dimensions $0.08 \times 0.03 \times 0.01$ mm was attached to a glass fiber using silicone grease. Data were collected on an Oxford Diffraction Xcalibur-3 diffractometer, equipped with a Sapphire CCD area detector, at 100 K, using a graphite monochromated Mo $K\alpha$ radiation. Complete crystal data and parameters for data collection and processing are listed in Table 1.



SCHEME 2: The up to now crystallographically established coordination modes of the sulfato ligand and the Harris notation [53] which describes these modes.

The structure was solved by direct methods using SIR92 [54] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [55]. Some residual electron density in the accessible voids of the structure was too disordered to refine as solvent molecules; therefore, the SQUEEZE procedure [56] of PLATON was employed to remove the

contribution of the electron density in the solvent region from the intensity data. The solvent-free model and intensity data were used for the final results reported here. The non-H atoms were treated anisotropically. The H atoms of the $(\text{py})_2\text{CNOH}$ ligands and the methyl groups of the methanol molecules were placed in calculated, ideal positions and

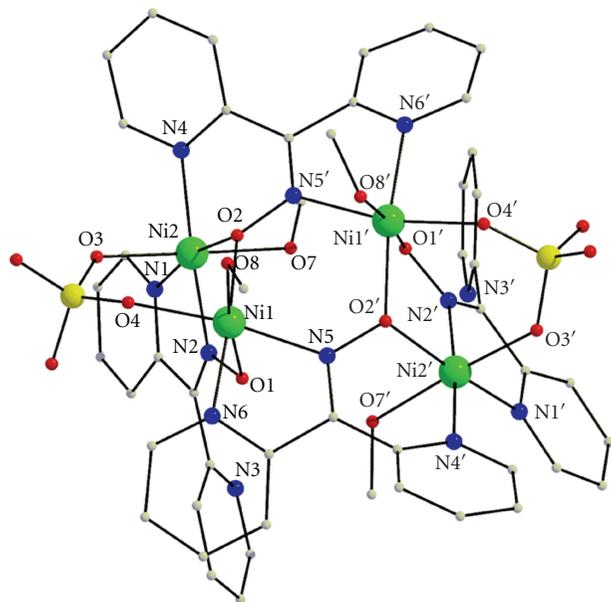


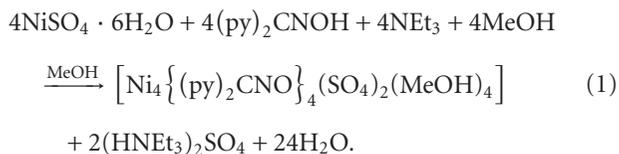
FIGURE 1: The molecular structure of **1**. H atoms have been omitted for clarity.

refined as riding on their respective C atoms. The H atom of the OH group of one independent methanol molecule (O(8)H) was located in difference Fourier maps and was refined isotropically, but the H atom of the OH group of the second independent methanol molecule (O(7)H) could not be located. The programs used were CRYSLIS CCD [57] for data collection, CRYSLIS RED [57] for cell and data refinement, WINGX [58] for crystallographic calculations, and MERCURY [59] and DIAMOND [60] for molecular graphics.

3. Results and Discussion

3.1. Synthetic Comments. Our general synthetic approach for the isolation of Ni^{II}/2-pyridyloximate/sulfato clusters has been to treat the metal sulfate “salt” with the appropriate ligand and a base in a variety of solvents. The addition of base is necessary for the deprotonation of the oxime ligand.

Treatment of NiSO₄·6H₂O with one equivalent of (py)₂CNOH and one equivalent of NEt₃ in MeOH gave a red solution which, upon crystallization, gave orange crystals of the new tetranuclear cluster which can be written as [Ni₄{(py)₂CNO}₄(SO₄)₂(MeOH)₄] (**1**). Its formation can be summarized in (1)



As expected, the nature of the base is not crucial for the identity of the product, and it affects only its crystallinity, and in some cases its purity; we were able to isolate **1** by using a plethora of different bases such as NaOMe, NMe₄OH,

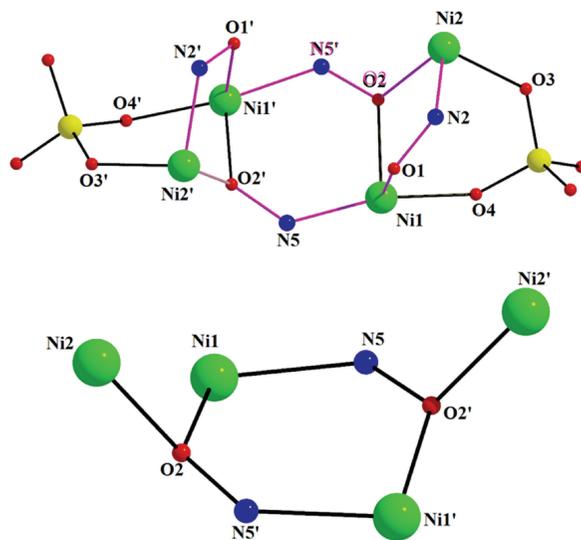


FIGURE 2: Top: the [Ni₄(μ-SO₄)₂(μ₂-ONR)₂(μ₃-ONR)₂] core of complex **1**, where R = -C(py)₂. The metallacrown-type ring is highlighted. Bottom: the core of **1** using only the μ₃ oximate groups.

NEt₄OH, and LiOH·H₂O. Small changes in the molar ratio of the reactants, the crystallization method, and the presence of counterions do not seem to affect the identity of the isolated product.

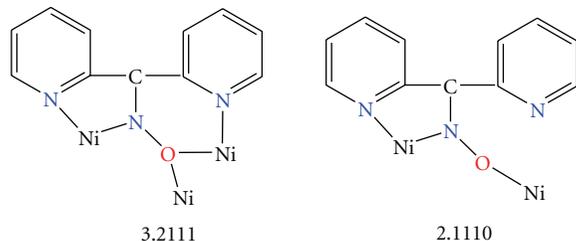
3.2. Description of Structure. Partially labeled plots of the complete structure and the core of the molecule [Ni₄{(py)₂CNO}₄(SO₄)₂(MeOH)₄] that is present in complex **1** are shown in Figures 1 and 2, respectively. Selected interatomic distances and angles are listed in Table 2.

The structure of **1** consists of tetranuclear molecules [Ni₄{(py)₂CNO}₄(SO₄)₂(MeOH)₄] which lie on a crystallographic inversion center. The metal ions are held together by two 3.2111 and two 2.1110 (using Harris notation, [53], Scheme 3) (py)₂CNO⁻ ligands, as well as two 2.1100 SO₄²⁻ ions. Four MeOH molecules act as terminal ligands and complete the coordination sphere of the four metal centers. The molecule has a metallacrown-type topology [61]. A *pseudo* 12-MC-4 ring forms; the *true* 12-MC-4 topology is “destroyed” by the bridging character of the oximate oxygen atoms O2 and O2’.

A distorted octahedral environment is created about each metal center; the chromophores are represented by the following formulas Ni(1,1’)(N_{py})(N_{ox})(O_{ox})₂(O_{sulf})(O_{met}) and Ni(2,2’)(N_{py})₂(N_{ox})(O_{ox})(O_{sulf})(O_{met}), where the abbreviations “py”, “ox”, “sulf” and “met” are for the 2-pyridyl, oximate, sulfato, and methanolic donor atoms, respectively. The average Ni–O_{ox}, Ni–N_{ox}, and Ni–N_{py} bond lengths of 2.054(3), 2.043(3), and 2.071(3) Å, respectively, agree well with the values expected for high-spin Ni^{II} ions in octahedral environment [34, 35, 62–64]. The Ni–O_{sulf} bond lengths are typical [41, 51, 62, 65]. The fact that S–(O3, O4) (average 1.474 Å) > S–(O5, O6) (average 1.450 Å) reflects the coordinating nature of O3 and O4 and the noncoordinating

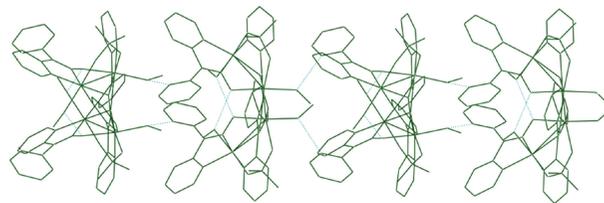
TABLE 2: Selected interatomic distances (Å) and angles (°) for **1**.

Ni1-O1	2.046 (3)	Ni2-O2	2.071 (3)
Ni1-O2	2.046 (3)	Ni2-O3	2.042 (3)
Ni1-O4	2.033 (3)	Ni2-O7	2.163 (3)
Ni1-O8	2.048 (3)	Ni2-N1	2.090 (3)
Ni1-N5	2.090 (3)	Ni2-N2	1.997 (4)
Ni1-N6	2.074 (3)	Ni2-N4	2.053 (3)
O1-Ni1-O2	89.59 (11)	O2-Ni2-O3	94.82 (11)
O1-Ni1-O4	101.65 (11)	O2-Ni2-O7	88.69 (10)
O1-Ni1-O8	173.53 (11)	O2-Ni2-N1	169.13 (12)
O1-Ni1-N5	82.89 (11)	O2-Ni2-N2	90.44 (12)
O1-Ni1-N6	83.38 (12)	O2-Ni2-N4	84.07 (12)
O2-Ni1-O4	84.24 (11)	O3-Ni2-O7	176.29 (10)
O2-Ni1-O8	88.62 (11)	O3-Ni2-N1	88.91 (12)
O2-Ni1-N5	107.12 (11)	O3-Ni2-N2	95.11 (12)
O2-Ni1-N6	170.67 (12)	O3-Ni2-N4	87.08 (12)
O4-Ni1-O8	84.36 (12)	O7-Ni2-N1	87.86 (11)
O4-Ni1-N5	167.92 (13)	O7-Ni2-N2	86.05 (12)
O4-Ni1-N6	91.16 (12)	O7-Ni2-N4	92.09 (12)
O8-Ni1-N5	91.70 (12)	N1-Ni2-N2	79.04 (13)
O8-Ni1-N6	99.02 (12)	N1-Ni2-N4	106.36 (13)
N5-Ni1-N6	78.16 (13)	N2-Ni2-N4	174.25 (13)

SCHEME 3: The two different coordination modes of the $(\text{py})_2\text{CNO}^-$ ligands present in complex **1** and the Harris notation [53] which describes them.

character of O5 and O6; as expected, the sulfur to “free” oxygen bond lengths are the shortest.

The crystal structure of **1** is stabilized by strong inter- and intramolecular hydrogen bonds. The intramolecular hydrogen bonds involve the O atom (O7 and its symmetry equivalent) belonging to a methanol ligand as donor and the O atom (O1 and its symmetry equivalent) of the doubly bridging organic ligand as acceptor [$\text{O1} \cdots \text{O7} = 2.721(3) \text{ \AA}$]. The O atom of the remaining methanol ligand (O8 and its symmetry equivalent) is participating as donor in an intermolecular hydrogen bond with the acceptor being the pyridyl N atom (N3 and its symmetry equivalent) of the doubly bridging organic ligand [$\text{O8} \cdots \text{N3} = 2.851(3) \text{ \AA}$, $\text{H}(\text{O8}) \cdots \text{N3} = 1.987(3) \text{ \AA}$, and $\text{O8-H}(\text{O8})-\text{N3} = 172.1(1)^\circ$]. This hydrogen bonding leads to the formation of a 1D chain along the *c* axis (Figure 3).

FIGURE 3: Representation of a part of the 1D chain formed in **1** along the *c* axis. The dotted lines represent H bonds.

The molecule of **1** contains the $[\text{Ni}_4(\mu\text{-SO}_4)_2(\mu_2\text{-ONR})_2(\mu_3\text{-ONR})_2]$ core, where $\text{R} = -\text{C}(\text{py})_2$ (Figure 2, top). An alternative description of the core (using only the μ_3 oximate groups) is $[\text{Ni}_4(\mu_3\text{-ONR})_2]^{6+}$ (Figure 2, bottom). The topology of the four Ni^{II} ions can be also described as “saddle-like,” and it is observed for the first time in Ni_4 clusters. The most common topologies of the metal ions in Ni_4^{II} complexes are the cubanes [66–73] and the face-shared distorted dicubanes in which one of the corners of each cubane is missing [74–79], while there are few Ni_4 clusters in which the metal ions adopt less common topologies such as linear [80–82], rectangular [83–87], and chair-like [88, 89] as follows.

Complex **1** joins a small but growing family of structurally characterized Ni(II) complexes containing the neutral or anionic forms of di-2-pyridyl ketone oxime as ligands [34, 36, 88–92]. The special features of **1** compared to the other members of this family are (1) It is the first example of these species containing the sulfato ligand, and (2) it has a unique Ni_4 clusters “saddle-like” metal topology.

3.3. IR Spectra. The medium intensity bands at 1568 and 1094 cm^{-1} in the spectrum of the free ligand $(\text{py})_2\text{CNOH}$ are assigned to $\nu(\text{C}=\text{N})_{\text{oxime}}$ and $\nu(\text{N}-\text{O})_{\text{oxime}}$ modes, respectively [51, 52, 93]. The 1094 cm^{-1} band is shifted to a higher wavenumber (1118 cm^{-1}) in **1**. This shift is in accord with the concept that upon deprotonation and oximate-O coordination, there is a higher contribution of $\text{N}=\text{O}$ to the electronic structure of the oximate group; consequently, the $\nu(\text{N}-\text{O})$ vibration shifts to a higher wavenumber in the complex relative to $(\text{py})_2\text{CNOH}$ [36]. Somewhat to our surprise, the 1568 cm^{-1} band is shifted to a higher wavenumber in the complex (1598 cm^{-1}), overlapping with an aromatic stretch. This shift may be indicative of the oxime nitrogen coordination [94]. Extensive studies on Schiff base complexes (which also contain a $\text{C}=\text{N}$ bond) have shown [95] that a change in the *s* character of the nitrogen lone pair occurs upon coordination such that the *s* character of nitrogen orbital involved in the $\text{C}=\text{N}$ bond increases; this change in hybridization produces a greater $\text{C}=\text{N}$ stretching force constant relative to the free neutral ligand.

The in-plane deformation band of the 2-pyridyl ring of free $(\text{py})_2\text{CNOH}$ at 622 cm^{-1} shifts upwards (641 cm^{-1}), confirming the involvement of the ring-N atom in coordination [96]. The presence of the 618 cm^{-1} band in the spectrum of **1** indicates that some 2-pyridyl rings are “free,” that is,

uncoordinated, in accordance with the $(\text{py})_2\text{CNO}^-$ ligands that are present in the complex.

The IR spectrum of the free, that is, ionic, sulfate (the ion belongs to the T_d point group) consists of two bands at ~ 1105 and $\sim 615\text{ cm}^{-1}$, assigned to the ν_3 (F_2) stretching [$\nu_d(\text{SO})$] and ν_4 (F_2) bending [$\delta_d(\text{OSO})$] modes, respectively [41, 97]. The ν_1 (A_1) stretching [$\nu_s(\text{SO})$] and ν_2 (E) bending [$\delta_d(\text{OSO})$] fundamentals are not IR active. The coordination of SO_4^{2-} to metal ions decreases the symmetry of the group, and the ν_3 and ν_4 modes are split [41, 97]. In the case when the SO_4^{2-} -site symmetry is lowered from T_d to C_{2v} (bidentate chelating or bridging coordination), which is the case in **1**, both ν_1 and ν_2 appear in the IR spectrum, while ν_3 and ν_4 each splits into three IR-active vibrations [97]. Thus, the bands at 1219 , 1130 , and 1020 cm^{-1} are attributed to the ν_3 modes [97], while the bands at 591 , 618 , and 670 cm^{-1} are assigned to the ν_4 modes [13, 74–79] with the intermediate wavenumber band being superimposed by a ligand's vibration. The band at 982 cm^{-1} and the weak feature at 452 cm^{-1} can be assigned [41, 97] to the ν_1 and ν_2 modes, respectively. These spectral features agree with the low C_{2v} symmetry for the sulfato ligand in the complex, as also confirmed crystallographically.

4. Conclusions

The present work extends the body of results that emphasize the ability of the sulfate ion to create unique structural types in 3d-metal cluster chemistry. The study of the coordination chemistry of the binary $\text{SO}_4^{2-}/(\text{py})_2\text{CNOH}$ ligand system in the presence of base in MeOH has provided access to the novel tetranuclear Ni(II) cluster $[\text{Ni}_4\{(\text{py})_2\text{CNO}\}_4(\text{SO}_4)_2(\text{MeOH})_4]$ (**1**). Complex **1** contains the $[\text{Ni}_4(\mu\text{-SO}_4)_2(\mu_2\text{-ONR})_2(\mu_3\text{-ONR})_2]$ core, where $\text{R} = \text{-C}(\text{py})_2$, with a unique saddle-like topology of the Ni^{II} ions; it is thus a valuable addition to the family of tetranuclear Ni^{II} clusters.

Analogues of **1** with 2-pyridinealdoxime $[(\text{py})\text{C}(\text{H})\text{NOH}]$, methyl(2-pyridyl)ketone oxime $[(\text{py})\text{C}(\text{Me})\text{NOH}]$, or phenyl(2-pyridyl)ketone oxime $[(\text{py})\text{C}(\text{ph})\text{NOH}]$ (Scheme 1) are not known, until to date, and further research efforts are in progress to determine the appropriate reaction conditions that could possibly favor such species. It is likely that the preparation and stability of such tetranuclear complexes are dependent on the particular nature of the R substituent on the oximate carbon. We are currently working on the chemistry of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}/(\text{py})\text{C}(\text{R})\text{NOH}$ ($\text{R} = \text{H, Me, Ph}$) reaction systems.

Supporting Information

CCDC 802606 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] V. Yu. Kukushkin and A. J. L. Pombeiro, "Oxime and oximate metal complexes: unconventional synthesis and reactivity," *Coordination Chemistry Reviews*, vol. 181, no. 1, pp. 147–175, 1999.
- [2] A. G. Smith, P. A. Tasker, and D. J. White, "The structures of phenolic oximes and their complexes," *Coordination Chemistry Reviews*, vol. 241, no. 1-2, pp. 61–85, 2003.
- [3] M. G. Davidson, A. L. Johnson, M. D. Jones, M. D. Lunn, and M. F. Mahon, "Titanium(IV) complexes of oximes—novel binding modes," *Polyhedron*, vol. 26, no. 5, pp. 975–980, 2007.
- [4] D. Mandal, V. Bertolasi, G. Aromí, and D. Ray, "A ketone oximate based cyclic cationic [Ni] inverse metallacrown from simultaneous chelation and bridging of two ligands," *Dalton Transactions*, no. 20, pp. 1989–1992, 2007.
- [5] C. P. Raptopoulou, A. K. Boudalis, Y. Sanakis et al., "Hexanuclear iron(III) salicylaldoximate complexes presenting the $[\text{Fe}_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2]^{12+}$ core: syntheses, crystal structures, and spectroscopic and magnetic characterization," *Inorganic Chemistry*, vol. 45, no. 5, pp. 2317–2326, 2006.
- [6] V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison et al., "Structural, magnetic and related attributes of some oximatebridged tetranuclear nickel(II) rhombs and a dinuclear congener," *Dalton Transactions*, no. 8, pp. 1587–1595, 2003.
- [7] D. T. Rosa, J. A. Krause Baue, and M. J. Baldwin, "Structural and spectroscopic studies of the versatile coordination chemistry of the chiral ligand N,N-bis(1-propan-2-onyl oxime)-L-methionine N'-methylamide with Ni and Zn," *Inorganic Chemistry*, vol. 40, no. 7, pp. 1606–1613, 2001.
- [8] M. J. Goldcamp, S. E. Robison, J. A. Krause Bauer, and M. J. Baldwin, "Oxygen reactivity of a Nickel(II)-polyoximate complex," *Inorganic Chemistry*, vol. 41, no. 9, pp. 2307–2309, 2002.
- [9] M. N. Kopylovich, V. Yu. Kukushkin, M. Haukka, J. J. R. Fraústo da Silva, and A. J. L. Pombeiro, "Zinc(II)/ketoxime system as a simple and efficient catalyst for hydrolysis of organonitriles," *Inorganic Chemistry*, vol. 41, no. 18, pp. 4798–4804, 2002.
- [10] S. Akine, T. Taniguchi, T. Saiki, and T. Nabeshima, "Ca- and Ba-selective receptors based on site-selective transmetalation of multinuclear polyoxime-zinc(II) complexes," *Journal of the American Chemical Society*, vol. 127, no. 2, pp. 540–541, 2005.
- [11] A. J. L. Pombeiro and V. Yu. Kukushkin, "Reactions of coordinated nitriles," in *Comprehensive Coordination Chemistry II*, J. A. McClevery and T. C. Meyer, Eds., vol. 1, pp. 631–637, Elsevier, Amsterdam, The Netherlands, 2004.
- [12] J. M. Thorpe, R. L. Beddoes, D. Collison et al., "Surface coordination chemistry: corrosion inhibition by tetranuclear cluster formation of iron with salicylaldoxime," *Angewandte Chemie—International Edition*, vol. 38, no. 8, pp. 1119–1121, 1999.
- [13] J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC, London, UK, 1993.
- [14] I. O. Fritsky, J. Swiatek-Kozłowska, A. Dobosz, T. Yu. Sliva, and N. M. Dudarenko, "Hydrogen bonded supramolecular structures of cationic and anionic module assemblies containing square-planar oximate complex anions," *Inorganica Chimica Acta*, vol. 357, no. 12, pp. 3746–3752, 2004.
- [15] S. Khanra, T. Weyhermüller, E. Rentschler, and P. Chaudhuri, "Self-assembly of a nonanuclear nickel(II) complex and its magnetic properties," *Inorganic Chemistry*, vol. 44, no. 23, pp. 8176–8178, 2005.

- [16] C. J. Milios, C. P. Raptopoulou, A. Terzis et al., "Hexanuclear manganese(III) single-molecule magnets," *Angewandte Chemie—International Edition*, vol. 43, no. 2, pp. 210–212, 2003.
- [17] J. P. Costes, F. Dahan, and A. Dupuis, "Is ferromagnetism an intrinsic property of the $\text{Cu}^{\text{II}}/\text{Gd}^{\text{III}}$ couple? 2. Structures and magnetic properties of novel trinuclear complexes with μ -phenolato- μ -oximate (Cu-Ln-Cu) cores ($\text{Ln} = \text{La, Ce, Gd}$)," *Inorganic Chemistry*, vol. 39, no. 26, pp. 5994–6000, 2000.
- [18] D. Robertson, J. F. Cannon, and N. Gerasimchuk, "Double-stranded metal-organic networks for one-dimensional mixed valence coordination polymers," *Inorganic Chemistry*, vol. 44, no. 23, pp. 8326–8342, 2005.
- [19] C. J. Milios, A. Vinslava, W. Wernsdorfer et al., "Spin switching via targeted structural distortion," *Journal of the American Chemical Society*, vol. 129, no. 20, pp. 6547–6561, 2007.
- [20] H. Miyasaka, R. Clérac, K. Mizushima et al., " $[\text{Mn}_2(\text{saltmen})_2\text{Ni}(\text{pao})_2(\text{L})_2](\text{A})_2$ with $\text{L} = \text{Pyridine, 4-picoline, 4-tert-butylpyridine, N-methylimidazole}$ and $\text{A} = \text{ClO}_4^-, \text{BF}_4^-, \text{PF}_6^-, \text{ReO}_4^-$: a family of single-chain magnets," *Inorganic Chemistry*, vol. 42, no. 25, pp. 8203–8213, 2003.
- [21] P. Chaudhuri, "Homo- and hetero-polymetallic exchange coupled metal-oximates," *Coordination Chemistry Reviews*, vol. 243, no. 1–2, pp. 143–190, 2003.
- [22] C. J. Milios, T. C. Stamatatos, and S. P. Perlepes, "The coordination chemistry of pyridyl oximes," *Polyhedron*, vol. 25, no. 1, pp. 134–194, 2006.
- [23] C. J. Milios, E. Kefalloniti, C. P. Raptopoulou et al., "Octanuclearity and tetradecanuclearity in manganese chemistry: an octanuclear manganese(II)/(III) complex featuring the novel $[\text{Mn}_8(\mu_4\text{-O})_2(\mu_3\text{-OH})_2]^{14+}$ core and $[\text{Mn}_{10}\text{Mn}_4\text{O}_4(\text{O}_2\text{CMe})_{20}\{(2-\text{py})_2\text{C}(\text{OH})\text{O}\}_4](2-\text{py} = 2-\text{pyridyl})$," *Chemical Communications*, vol. 9, no. 7, pp. 819–821, 2003.
- [24] C. J. Milios, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, and S. P. Perlepes, "Di-2-pyridyl ketone oxime in 3d-metal carboxylate cluster chemistry: a new family of mixed-valence MnMn complexes," *Inorganic Chemistry Communications*, vol. 6, no. 8, pp. 1056–1060, 2003.
- [25] C. J. Milios, T. C. Stamatatos, P. Kyritsis et al., "Phenyl 2-pyridyl ketone and its oxime in manganese carboxylate chemistry: synthesis, characterisation, X-ray studies and magnetic properties of mononuclear, trinuclear and octanuclear complexes," *European Journal of Inorganic Chemistry*, no. 14, pp. 2885–2901, 2004.
- [26] C. J. Milios, E. Kefalloniti, C. P. Raptopoulou et al., "2-Pyridinealdoxime $[(\text{py})\text{CHNOH}]$ in manganese(II) carboxylate chemistry: mononuclear, dinuclear, tetranuclear and polymeric complexes, and partial transformation of $(\text{py})\text{CHNOH}$ to picolinate(-1)," *Polyhedron*, vol. 23, no. 1, pp. 83–95, 2004.
- [27] M. Alexiou, E. Katsoulakou, C. Dendrinou-Samara et al., "Di-2-pyridyl ketone oxime in zinc chemistry: inverse 12-metallacrown-4 complexes and cationic pentanuclear clusters," *European Journal of Inorganic Chemistry*, no. 10, pp. 1964–1978, 2005.
- [28] T. C. Stamatatos, S. Dionyssopoulou, G. Efthymiou et al., "The first cobalt metallacrowns: preparation and characterization of mixed-valence cobalt(II/III), inverse 12-metallacrown-4 complexes," *Inorganic Chemistry*, vol. 44, no. 10, pp. 3374–3376, 2005.
- [29] T. C. Stamatatos, A. K. Boudalis, Y. Sanakis, and C. P. Raptopoulou, "Reactivity and structural and physical studies of tetranuclear iron(III) clusters containing the $[\text{Fe}(\mu\text{-O})$ "butterfly" core: an Fe cluster with an $S = 1$ ground state," *Inorganic Chemistry*, vol. 45, no. 18, pp. 7372–7381, 2006.
- [30] T. C. Stamatatos, J. C. Vlahopoulou, Y. Sanakis et al., "Formation of the $\{\text{Cu}_3^{\text{II}}(\mu_3\text{-OH})\}^{5+}$ core in copper(II) carboxylate chemistry via use of di-2-pyridyl ketone oxime $[(\text{py})_2\text{CNOH}]$: $[\text{Cu}_3(\text{OH})(\text{O}_2\text{CR})_2\{(\text{py})_2\text{CNO}\}_3]$ ($\text{R} = \text{Me, Ph}$)," *Inorganic Chemistry Communications*, vol. 9, no. 8, pp. 814–818, 2006.
- [31] C. Papatriantafyllopoulou, C. P. Raptopoulou, A. Escuer, and C. J. Milios, "A rare all-Mn decametallacage from distorted face-sharing cubes," *Inorganica Chimica Acta*, vol. 360, no. 1, pp. 61–68, 2007.
- [32] K. V. Pringouri, C. P. Raptopoulou, A. Escuer, and T. C. Stamatatos, "Initial use of di-2-pyridyl ketone oxime in chromium carboxylate chemistry: triangular Cr ($\mu\text{-O}$) compounds and unexpected formation of a carboxylate-free dichromium(II,II) complex," *Inorganica Chimica Acta*, vol. 360, no. 1, pp. 69–83, 2007.
- [33] T. C. Stamatatos, D. Foguet-Albiol, C. C. Stoumpos et al., "New Mn structural motifs in manganese single-molecule magnetism from the use of 2-pyridyloximate ligands," *Polyhedron*, vol. 26, no. 9–11, pp. 2165–2168, 2007.
- [34] T. C. Stamatatos, E. Diamantopoulou, C. P. Raptopoulou, V. Psycharis, A. Escuer, and S. P. Perlepes, "Acetate/di-2-pyridyl ketone oximate "blend" as a source of high-nuclearity nickel(II) clusters: dependence of the nuclearity on the nature of the inorganic anion present," *Inorganic Chemistry*, vol. 46, no. 7, pp. 2350–2352, 2007.
- [35] T. C. Stamatatos, C. Papatriantafyllopoulou, E. Katsoulakou, C. P. Raptopoulou, and S. P. Perlepes, "2-Pyridyloximate clusters of cobalt and nickel," *Polyhedron*, vol. 26, no. 9–11, pp. 1830–1834, 2007.
- [36] T. C. Stamatatos, A. Escuer, K. A. Abboud, C. P. Raptopoulou, S. P. Perlepes, and G. Christou, "Unusual structural types in nickel cluster chemistry from the use of pyridyl oximes: Ni, NiNa, and Ni clusters," *Inorganic Chemistry*, vol. 47, no. 24, pp. 11825–11838, 2008.
- [37] M. Murugesu, K. A. Abboud, and G. Christou, "New hexanuclear and dodecanuclear Fe(III) clusters with carboxylate and alkoxide-based ligands from cluster aggregation reactions," *Polyhedron*, vol. 23, no. 17, pp. 2779–2788, 2004.
- [38] T. Afrati, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, V. Tangoulis, and D. P. Kessissoglou, "A tetranuclear mixed-valent MnMn compound with a $(\mu\text{-O})\text{Mn}$ core," *Angewandte Chemie—International Edition*, vol. 41, no. 12, pp. 2148–2150, 2002.
- [39] A. J. Stemmler, J. W. Kampf, and V. L. Pecoraro, "Synthesis and crystal structure of the first inverse 12-metallacrown-4," *Inorganic Chemistry*, vol. 34, no. 9, pp. 2271–2272, 1995.
- [40] T. C. Stamatatos, D. Foguet-Albiol, C. C. Stoumpos et al., "Initial example of a triangular single-molecule magnet from ligand-induced structural distortion of a $[\text{MnO}]$ complex," *Journal of the American Chemical Society*, vol. 127, no. 44, pp. 15380–15381, 2005.
- [41] C. Papatriantafyllopoulou, E. Manessi-Zoupa, A. Escuer, and S. P. Perlepes, "The sulfate ligand as a promising "player" in 3d-metal cluster chemistry," *Inorganica Chimica Acta*, vol. 362, no. 3, pp. 634–650, 2009.
- [42] M. I. Khan, S. Cevik, and R. J. Doedens, "Inorganic-organic hybrids derived from oxovanadium sulfate motifs: synthesis and characterization of $[\text{VO}(\mu\text{-SO})(2,2'\text{-bpy})]_{\infty}$," *Chemical Communications*, no. 19, pp. 1930–1931, 2001.

- [43] A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Côté, J. Kim, and O. M. Yaghi, "Design, synthesis, structure, and gas (N, Ar, CO, CH, and H) sorption properties of porous metal-organic tetrahedral and heterocuboidal polyhedra," *Journal of the American Chemical Society*, vol. 127, no. 19, pp. 7110–7118, 2005.
- [44] J. Moriyama, H. Nishiguchi, T. Ishihara, and Y. Takita, "Metal sulfate catalyst for CCl_2F_2 decomposition in the presence of H_2O ," *Industrial and Engineering Chemistry Research*, vol. 41, no. 1, pp. 32–36, 2002.
- [45] S. Y. Wan, Y. Z. Li, T. A. Okamura, J. Fan, W. Y. Sun, and N. Ueyama, "Syntheses, structures, and properties of two-dimensional honeycomb networks from the assembly of the tripodal ligand 2,4,6-Tris[4-(imidazol-1-ylmethyl)phenyl]-1,3,5-triazine with metal salts," *European Journal of Inorganic Chemistry*, no. 20, pp. 3783–3789, 2003.
- [46] Z. He, E. N. Q. Gao, Z. M. Wang, C. H. Yan, and M. Kurmoo, "Coordination polymers based on inorganic lanthanide(III) sulfate skeletons and an organic isonicotinate N-oxide connector: segregation into three structural types by the lanthanide contraction effect," *Inorganic Chemistry*, vol. 44, no. 4, pp. 862–874, 2005.
- [47] J. Reedijk, "The relevance of hydrogen bonding in the mechanism of action of platinum antitumor compounds," *Inorganica Chimica Acta*, vol. 198–200, pp. 873–881, 1992.
- [48] D. Peak, R. G. Ford, and D. L. Sparks, "An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite," *Journal of Colloid and Interface Science*, vol. 218, no. 1, pp. 289–299, 1999.
- [49] G. Tamasi and R. Cini, "Study of binary and ternary metal complexes containing the sulfato ligand: molecular models for selected non-catalytic sites in sulfurylase," *Dalton Transactions*, no. 14, pp. 2928–2936, 2003.
- [50] C. Papatriantafyllopoulou, L. F. Jones, T. D. Nguyen et al., "Using pyridine amidoximes in 3d-metal cluster chemistry: a novel ferromagnetic Ni complex from the use of pyridine-2-amidoxime," *Dalton Transactions*, no. 24, pp. 3153–3155, 2008.
- [51] C. Papatriantafyllopoulou, G. Aromi, A. J. Tasiopoulos et al., "Use of the sulfato ligand in 3d-metal cluster chemistry: a family of hexanuclear nickel(II) complexes with 2-pyridyl-substituted oxime ligands," *European Journal of Inorganic Chemistry*, no. 18, pp. 2761–2774, 2007.
- [52] C. G. Efthymiou, A. A. Kitos, C. P. Raptopoulou, S. P. Perlepes, A. Escuer, and C. Papatriantafyllopoulou, "Employment of the sulfate ligand in 3d-metal cluster chemistry: a novel hexanuclear nickel(II) complex with a chair metal topology," *Polyhedron*, vol. 28, no. 15, pp. 3177–3184, 2009.
- [53] R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, and R. E. P. Winpenny, "Inter-ligand reactions: in situ formation of new polydentate ligands," *Journal of the Chemical Society, Dalton Transactions*, no. 14, pp. 2349–2356, 2000.
- [54] A. Altomare, G. Cascarano, C. Giacovazzo et al., "SIR92—a program for automatic solution of crystal structures by direct methods," *Journal of Applied Crystallography*, vol. 27, p. 435, 1993.
- [55] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, Göttingen, Germany, 1997.
- [56] P. Van der Sluis and A. L. Spek, "BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions," *Foundations of Crystallography*, vol. 46, no. 4, pp. 194–201, 1990.
- [57] Oxford Diffraction, CrysAlis CCD and CrysAlis RED, version 1.171.32.15; Oxford Diffraction Ltd, Abingdon, UK, 2008.
- [58] L. J. Farrugia, "WinGX suite for small-molecule single-crystal crystallography," *Journal of Applied Crystallography*, vol. 32, no. 4, pp. 837–838, 1999.
- [59] I. J. Bruno, J. C. Cole, P. R. Edgington et al., "New software for searching the Cambridge Structural Database and visualizing crystal structures," *Acta Crystallographica Section B*, vol. 58, no. 3, pp. 389–397, 2002.
- [60] K. Bradenburg, *DIAMOND, Release 3.1f, Crystal Impact*, GbR, Bonn, Germany, 2008.
- [61] V. L. Pecoraro, A. J. Stemmler, B. R. Gibney et al., "Metallacrowns: a new class of molecular recognition agents," *Progress in Inorganic Chemistry*, vol. 45, pp. 83–177, 1997.
- [62] C. Papatriantafyllopoulou, C. G. Efthymiou, C. P. Raptopoulou et al., "Initial use of the di-2-pyridyl ketone/sulfate "blend" in 3d-metal cluster chemistry: preparation, X-ray structures and physical studies of zinc(II) and nickel(II) cubanes," *Journal of Molecular Structure*, vol. 829, no. 1–3, pp. 176–188, 2007.
- [63] G. S. Papaefstathiou, A. Escuer, F. A. Mautner et al., "Use of the di-2-pyridyl ketone/acetate/dicyanamide "blend" in manganese(II), cobalt(II) and nickel(II) chemistry: neutral cubane complexes," *European Journal of Inorganic Chemistry*, no. 5, pp. 879–893, 2005.
- [64] C. G. Efthymiou, C. P. Raptopoulou, A. Terzis et al., "A systematic exploration of nickel(II)/acetate/di-2-pyridyl ketone chemistry: neutral and cationic tetranuclear clusters, and a novel mononuclear complex," *European Journal of Inorganic Chemistry*, no. 11, pp. 2236–2252, 2006.
- [65] C. Papatriantafyllopoulou, C. P. Raptopoulou, A. Terzis, J. F. Janssens, S. P. Perlepes, and E. Manessi-Zoupa, "Reactions of nickel(II) sulfate hexahydrate with methyl(2-pyridyl)ketone oxime: two mononuclear sulfato complexes containing the neutral ligand," *Zeitschrift für Naturforschung*, vol. 62, no. 9, pp. 1123–1132, 2007.
- [66] M. Moragues-Cánovas, M. Helliwell, L. Ricard et al., "An Ni, single-molecule magnet: synthesis, structure and low-temperature magnetic behavior," *European Journal of Inorganic Chemistry*, no. 11, pp. 2219–2222, 2004.
- [67] E. N. C. Yang, W. Wernsdorfer, S. Hill et al., "Exchange bias in Ni single-molecule magnets," *Polyhedron*, vol. 22, no. 14–17, pp. 1727–1733, 2003.
- [68] A. Escuer, M. Font-Bardía, S. B. Kumar, X. Solans, and R. Vicente, "Two new nickel(II) cubane compounds derived from pyridine-2-methoxide (Pym): $\text{Ni}(\text{Pym})\text{Cl}(\text{CHOH})$ and $\text{Ni}(\text{Pym})(\text{N})(\text{CH OH})$. Crystal structures and magnetic properties," *Polyhedron*, vol. 18, no. 6, pp. 909–914, 1999.
- [69] E. N. C. Yang, W. Wernsdorfer, L. N. Zakharov et al., "Fast magnetization tunneling in tetranickel(II) single-molecule magnets," *Inorganic Chemistry*, vol. 45, no. 2, pp. 529–546, 2006.
- [70] C. G. Efthymiou, C. P. Raptopoulou, A. Terzis et al., "A systematic exploration of nickel(II)/acetate/di-2-pyridyl ketone chemistry: neutral and cationic tetranuclear clusters, and a novel mononuclear complex," *European Journal of Inorganic Chemistry*, no. 11, pp. 2236–2252, 2006.
- [71] C. G. Efthymiou, C. Papatriantafyllopoulou, N. I. Alexopoulos et al., "A mononuclear complex and a cubane cluster from the initial use of 2-(hydroxymethyl)pyridine in nickel(II) carboxylate chemistry," *Polyhedron*, vol. 28, no. 15, pp. 3373–3381, 2009.

- [72] A. Sieber, C. Boskovic, R. Bircher et al., "Synthesis and spectroscopic characterization of a new family of Ni spin clusters," *Inorganic Chemistry*, vol. 44, no. 12, pp. 4315–4325, 2005.
- [73] K. Isele, F. Gigon, A. F. Williams et al., "Synthesis, structure and properties of $\{M_4O_4\}$ cubanes containing nickel(II) and cobalt(II)," *Dalton Transactions*, no. 3, pp. 332–341, 2007.
- [74] M. A. Halcrow and G. Christou, "Biomimetic chemistry of nickel," *Chemical Reviews*, vol. 94, no. 8, pp. 2421–2481, 1994.
- [75] A. J. Edwards, B. F. Hoskins, E. H. Kachab, A. Markiewicz, K. S. Murray, and R. Robso, "Synthesis, x-ray crystal structures, and magnetic properties of Ni complexes of a macrocyclic tetranucleating ligand," *Inorganic Chemistry*, vol. 31, no. 17, pp. 3585–3591, 1992.
- [76] E. Jabri, M. B. Carr, R. P. Hausinger, and P. A. Karplus, "The crystal structure of urease from *Klebsiella aerogenes*," *Science*, vol. 268, no. 5213, pp. 998–1004, 1995.
- [77] A. Escuer, R. Vicente, S. B. Kumar, and F. A. Mautner, "Spin frustration in the butterfly-like tetrameric $[Ni(\mu-CO)(aetpy)]_4[ClO_4]_2$ [aetpy = (2-aminoethyl)pyridine] complex. Structure and magnetic properties," *Journal of the Chemical Society—Dalton Transactions*, no. 20, pp. 3473–3477, 1998.
- [78] J. M. Clemente, H. Andres, J. J. Borrás-Almenar et al., "Magnetic excitations in polyoxometalate clusters observed by inelastic neutron scattering: evidence for ferromagnetic exchange interactions and spin anisotropy in the tetrameric nickel(II) cluster $[Ni(HO)(PWO)]_4$ and comparison with the magnetic properties," *Journal of the American Chemical Society*, vol. 121, no. 43, pp. 10021–10027, 1999.
- [79] Z. E. Serna, L. Lezama, M. K. Urriaga et al., "A dicubane-like tetrameric nickel(II) azido complex," *Angewandte Chemie—International Edition*, vol. 39, no. 2, pp. 344–347, 2000.
- [80] P. Venkateswara Rao, S. Bhaduri, J. Jiang, and R. H. Holm, "Sulfur bridging interactions of cis-planar Ni-S N coordination units with nickel(II), copper(I,II), zinc(II), and mercury(II): a library of bridging modes, including Ni (μ -SR)M rhombs," *Inorganic Chemistry*, vol. 43, no. 19, pp. 5833–5849, 2004.
- [81] K. T. Szacilowski, P. Xie, A. Y. S. Malkhasian et al., "Solid-state structures and magnetic properties of halide-bridged, face-to-face bis-nickel(II)-macrocyclic ligand complexes: ligand-mediated interchanges of electronic configuration," *Inorganic Chemistry*, vol. 44, no. 17, pp. 6019–6033, 2005.
- [82] X. López, M. Y. Huang, G. C. Huang et al., "Even-numbered metal chain complexes: synthesis, characterization, and DFT analysis of $[Ni(\mu-Tsdpda)(H_2O)]_n$ ($Tsdpda = N$ -(*p*-toluenesulfonyl) dipyridyldiamido), $[Ni(\mu-Tsdpda)]_n$, and related Ni string complexes," *Inorganic Chemistry*, vol. 45, no. 22, pp. 9075–9084, 2006.
- [83] E. Carmona, E. Gutiérrez-Puebla, A. Monge, M. Paneque, and M. L. Poveda, "Unusual alkylidene-bridged complexes of nickel by α -H abstraction from a nickelacycle. Crystal and molecular structure of $[Ni(CHCMe-o-CH)Cl(PMe_3)]_2$," *Journal of the Chemical Society, Chemical Communications*, no. 3, pp. 148–150, 1991.
- [84] J. Klingele, J. F. Boas, J. R. Pilbrow et al., "A $[2 \times 2]$ nickel(II) grid and a copper(II) square result from differing binding modes of a pyrazine-based diamide ligand," *Dalton Transactions*, no. 6, pp. 633–645, 2007.
- [85] F. Meyer, M. Konrad, and E. Kaifer, "Novel μ -coordination of urea at a nickel(II) site: structure, reactivity and ferromagnetic superexchange," *European Journal of Inorganic Chemistry*, no. 11, pp. 1851–1854, 1999.
- [86] K. Yamada, S. Yagishita, H. Tanaka et al., "Metal-complex assemblies constructed from the flexible hinge-like ligand-Hbhnq: structural versatility and dynamic behavior in the solid state," *Chemistry—A European Journal*, vol. 10, no. 11, pp. 2647–2660, 2004.
- [87] M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab, and R. Robson, "Synthesis and X-ray crystal structures of Ni and Zn complexes of a macrocyclic tetranucleating ligand," *Journal of the American Chemical Society*, vol. 111, no. 10, pp. 3603–3610, 1989.
- [88] M. Alexiou, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, V. Tangoulis, and D. P. Kessissoglou, "A cationic tetranuclear $[Ni(MeOH)(pko)]_4$ cluster showing antiferro- and ferromagnetic features," *European Journal of Inorganic Chemistry*, no. 19, pp. 3822–3827, 2004.
- [89] V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison et al., "A tetrameric nickel(II) "chair" with both antiferromagnetic internal coupling and ferromagnetic spin alignment," *Angewandte Chemie—International Edition*, vol. 40, no. 24, pp. 4734–4737, 2001.
- [90] G. Psomas, C. Dendrinou-Samara, M. Alexiou et al., "The first fused dimer metallacrown $Ni_2^{II}(mcpa)_2(CH_3OH)_3(H_2O)[12-MC_{Ni^{II}N_{(shi)2}(pko)2}-4][12-MC_{Ni^{II}N_{(shi)3}(pko)-4}]$," *Inorganic Chemistry*, vol. 37, no. 26, pp. 6556–6557, 1998.
- [91] G. Psomas, A. J. Stemmler, C. Dendrinou-Samara et al., "Preparation of site-differentiated mixed ligand and mixed ligand/mixed metal metallacrowns," *Inorganic Chemistry*, vol. 40, no. 7, pp. 1562–1570, 2001.
- [92] M. Alexiou, I. Tsivikas, C. Dendrinou-Samara et al., "High nuclearity nickel compounds with three, four or five metal atoms showing antibacterial activity," *Journal of Inorganic Biochemistry*, vol. 93, no. 3-4, pp. 256–264, 2003.
- [93] P. Chaudhuri, M. Winter, U. Flörke, and H. J. Haupt, "An effectively diamagnetic oximate-bridged asymmetric dinuclear copper(II) complex with a Cu(II)I bond," *Inorganica Chimica Acta*, vol. 232, no. 1-2, pp. 125–130, 1995.
- [94] C. Papatriantafyllopoulou, C. P. Raptopoulou, A. Terzis, E. Manessi-Zoupa, and S. P. Perlepes, "Investigation of the zinc chloride/methyl(2-pyridyl)ketone oxime reaction system: a mononuclear complex and an inverse 12-metallacrown-4 cluster," *Zeitschrift für Naturforschung*, vol. 61, no. 1, pp. 37–46, 2006.
- [95] J. J. López-Garriga, G. T. Babcock, and J. F. Harrison, "Factors influencing the C=N stretching frequency in neutral and protonated Schiff's bases," *Journal of the American Chemical Society*, vol. 108, no. 23, pp. 7241–7251, 1986.
- [96] A. B. P. Lever and E. Mantovani, "The far-infrared and electronic spectra of some bis-ethylenediamine and related complexes of copper(II) and the relevance of these data to tetragonal distortion and bond strengths," *Inorganic Chemistry*, vol. 10, no. 4, pp. 817–826, 1971.
- [97] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, NY, USA, 4th edition, 1986.



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