

Reactions of Nickel(II) Sulfate Hexahydrate with Methyl(2-pyridyl)ketone Oxime: Two Mononuclear Sulfato Complexes Containing the Neutral Ligand

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Z. Naturforsch. **2007**, 62b, 1123–1132; received March 16, 2007

In dedication to Professor Herman O. Desseyn on the occasion of his retirement and for his important contributions to Vibrational Spectroscopy and Coordination Chemistry

The reactions of methyl(2-pyridyl)ketone oxime, (py)C(Me)NOH, with nickel(II) sulfate hexahydrate, in the absence of an external base, have been investigated. The reaction between equimolar quantities of NiSO₄ · 6 H₂O and (py)C(Me)NOH in H₂O leads to the mononuclear complex [Ni(SO₄){(py)C(Me)NOH}(H₂O)₃] · H₂O (**1** · H₂O), while an excess of the organic ligand affords the 1 : 2 compound [Ni(SO₄){(py)C(Me)NOH}₂(H₂O)] · H₂O (**2** · H₂O). The structures of both compounds have been determined by single crystal X-ray diffraction. In both complexes the organic ligand chelates through its nitrogen atoms and the sulfate anion acts as a monodentate ligand. The thermal decomposition of complexes **1** · H₂O and **2** · H₂O has been studied. The IR data are discussed in terms of the nature of bonding and the structures of the two complexes.

Key words: Crystal Structures, Infrared Spectra, Methyl(2-pyridyl)ketone Oxime Complexes, Nickel(II) Complexes, Sulfate Ligand

Introduction

There is currently a renewed interest in the coordination chemistry of oximes [1]. The research efforts are driven by a number of considerations. These include the solution of pure chemical problems [2–4], the desire to provide useful bioinorganic models (oximes may be considered to be reasonable models for the biologically significant imidazole donor group of the amino acid histidine) [5], the development of new oxygen activation catalysts based on nickel(II) polyoximate complexes [6], the application of metal ion/oxime systems as efficient catalysts for the hydrolysis of organonitriles [7] (metal ions can behave as extremely strong activators of RCN molecules towards nucleophilic attack by OH[−]/H₂O), the design of Ca²⁺- and Ba²⁺-selective receptors based on site-selective transmetallation of polynuclear zinc(II)/polyoxime complexes [8], the study of metal ion-assisted organic transformations [9], the mecha-

nistic investigation of corrosion inhibition by Acorga P5000 (a modern corrosion inhibitor comprising 5-nonylsalicylaldoxime as a mixture of carbon chain isomers) on iron surfaces [10], and the employment of oximate ligands in the synthesis of homo- [1, 11] and heterometallic [1, 12] clusters and coordination polymers [13] with interesting magnetic properties, including single-molecule magnetism [14–17] and single-chain magnetism [18].

Ligands containing one oxime group and one pyridyl group, without other donor sites, are popular in coordination chemistry. Most of these ligands contain a 2-pyridyl group, and thus are named 2-pyridyl oximes, (py)C(R)NOH (Fig. 1). The anionic forms of these molecules, (py)C(R)NO[−], are versatile ligands for a variety of research objectives, including μ_2 and μ_3 behaviour [1, 11]; the activation of 2-pyridyl oximes by 3d metal centers towards further reactions is also becoming a fruitful area of research [11]. The majority of the metal complexes of these ligands have been pre-

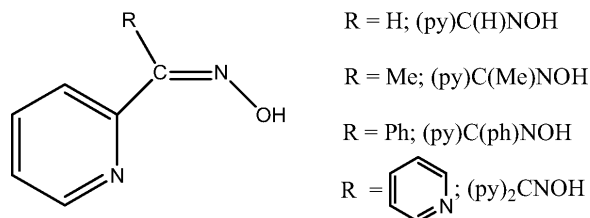


Fig. 1. General structural formula and abbreviations of simple 2-pyridyl oximes, including methyl(2-pyridyl)ketone oxime [(py)C(Me)NOH].

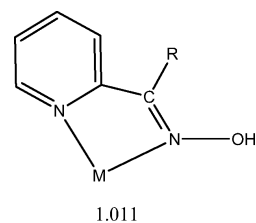


Fig. 2. The common coordination mode of the neutral 2-pyridyl oximes and the Harris notation [21] describing it.

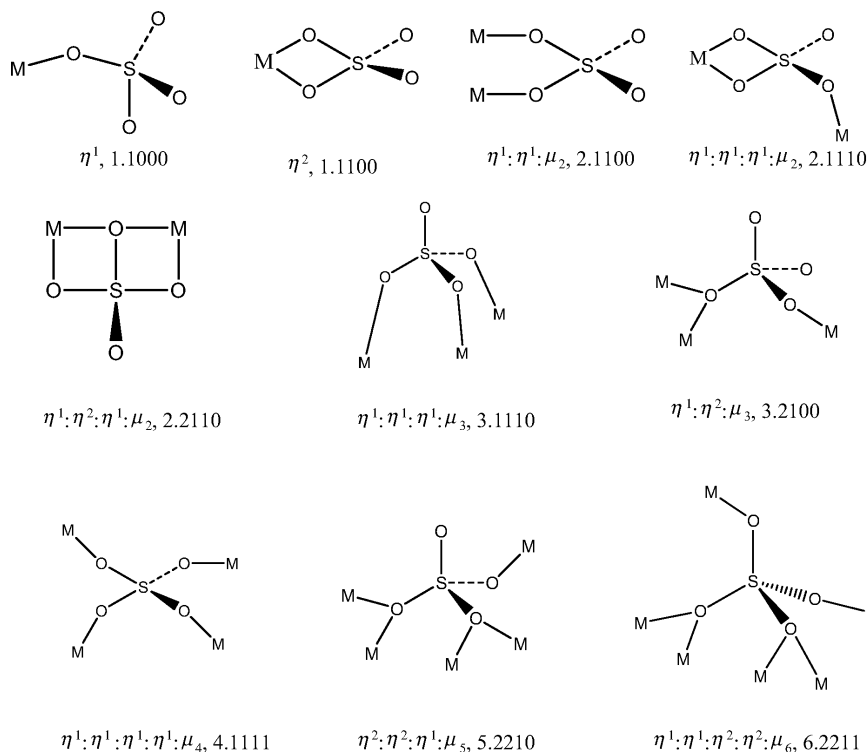


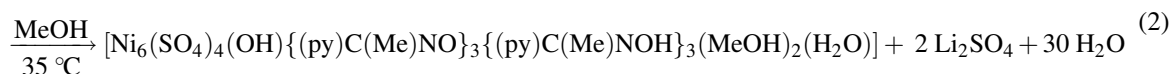
Fig. 3. The crystallographically established coordination modes of the sulfato ligand, and the η/μ and Harris notations [21] describing them.

pared in the last 15 years and much of their chemistry remains to be explored in more detail [1, 11].

With only two exceptions [19,20], the hitherto structurally characterized metal complexes containing *neutral* 2-pyridyl oximes as ligands are *mononuclear*. The donor atoms of the neutral 2-pyridyl oximes in metal complexes are the nitrogen atom of the oxime group and the nitrogen atom of the pyridyl group. Thus, (py)C(R)NOH behaves as an *N,N'*-chelating ligand (see Fig. 2) making necessary the employment of additional inorganic or organic anions to complete the coordination sphere of the metal center or to balance the charge of the complex cation. A variety of *monoanions* have been used for this reason,

e. g. PhCO_2^- [22,23], Cl^- [20,24,25], Br^- [26] and NO_3^- [27]. Recently, we have started a research program to explore the use of the sulfate ion, SO_4^{2-} , in 3d metal/2-pyridyl oxime chemistry, instead of the above mentioned *monoanionic* ligands. The possible advantages of using SO_4^{2-} include (i) the possibility of triggering aggregation of preformed smaller species into new products, and (ii) the possible diversion of known reaction systems developed using inorganic *monoanions* to new species as a result of the higher charge and higher denticity of the sulfate ligand.

The sulfate ion is currently a ligand of intense interest [28–34]. The μ_2 , μ_3 , μ_4 , μ_5 or μ_6 potential of SO_4^{2-} (Fig. 3) [28, 29] prompted us to combine 2-



pyridyloximes with the sulfate ligand to generate new types of compounds.

In this work we report on the synthesis and X-ray structural characterization of two new sulfato Ni(II) complexes, $[\text{Ni}(\text{SO}_4)\{(\text{py})\text{C}(\text{Me})\text{NOH}\}(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ ($\mathbf{1} \cdot \text{H}_2\text{O}$) and $[\text{Ni}(\text{SO}_4)\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ ($\mathbf{2} \cdot \text{H}_2\text{O}$), which contain the neutral methyl(2-pyridyl)ketone oxime as an organic ligand. The two complexes have also been characterized by thermal techniques and IR spectroscopy.

Results and Discussion

Brief synthetic comments

The chemical and structural identity of the products from the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}/(\text{py})\text{C}(\text{Me})\text{NOH}$ reaction system in H_2O depends on the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O} : (\text{py})\text{C}(\text{Me})\text{NOH}$ ratio. Treatment of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ with one equivalent of $(\text{py})\text{C}(\text{Me})\text{NOH}$ leads to the isolation of complex $\mathbf{1}$, while treatment of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ with three equivalents of $(\text{py})\text{C}(\text{Me})\text{NOH}$ leads to complex $\mathbf{2}$.

Two features of the reactions deserve comments. First, the “wrong” $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ to $(\text{py})\text{C}(\text{Me})\text{NOH}$ reaction ratio (1 : 3) employed for the preparation of $\mathbf{2} \cdot \text{H}_2\text{O}$ (see Experimental Section) did not prove detrimental to the formation of the complex. With the identity of $\mathbf{2} \cdot \text{H}_2\text{O}$ established by single-crystal X-ray crystallography, the “correct” stoichiometry was employed and led to the pure compound in high yield. Second, the presence of two oxime ligands per Ni^{II} in $\mathbf{2} \cdot \text{H}_2\text{O}$ has as a result the participation of only one H_2O molecule (instead of three in $\mathbf{1} \cdot \text{H}_2\text{O}$) in the coordination sphere of the metal ion, as expected.

The fact that complexes $\mathbf{1} \cdot \text{H}_2\text{O}$ and $\mathbf{2} \cdot \text{H}_2\text{O}$ contain basically the same ligand set (the major difference being the number of the coordinated $(\text{py})\text{C}(\text{Me})\text{NOH}$ molecules) led us to suspect that $\mathbf{1} \cdot \text{H}_2\text{O}$ could be transformed into $\mathbf{2} \cdot \text{H}_2\text{O}$ by addition of the ligand; this has, indeed, turned out to be the case. Treatment of $\mathbf{1} \cdot \text{H}_2\text{O}$ with one equivalent of $(\text{py})\text{C}(\text{Me})\text{NOH}$ in MeCN leads to high yield formation (> 70 %) of pure $\mathbf{2} \cdot \text{H}_2\text{O}$ (see eq. (1)).

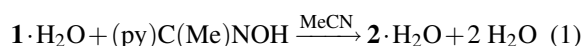


Table 1. Selected bond lengths (Å) and angles (deg) relevant to the nickel coordination sphere in $\mathbf{1} \cdot \text{H}_2\text{O}$.

Ni–O(11)	2.062(2)	Ni–N(2)	2.076(2)
Ni–OW(1)	2.071(2)	S–O(11)	1.482(2)
Ni–OW(2)	2.100(2)	S–O(12)	1.478(2)
Ni–OW(3)	2.024(2)	S–O(13)	1.463(2)
Ni–N(1)	2.072(2)	S–O(14)	1.475(2)
O(11)–Ni–OW(1)	86.8(1)	OW(1)–Ni–N(2)	88.0(1)
O(11)–Ni–OW(2)	90.4(1)	OW(2)–Ni–OW(3)	91.6(1)
O(11)–Ni–OW(3)	92.2(1)	OW(2)–Ni–N(1)	87.5(1)
O(11)–Ni–N(1)	170.4(1)	OW(2)–Ni–N(2)	89.1(1)
O(11)–Ni–N(2)	93.1(1)	OW(3)–Ni–N(1)	97.3(1)
OW(1)–Ni–OW(2)	175.8(1)	OW(3)–Ni–N(2)	174.6(1)
OW(1)–Ni–OW(3)	91.6(1)	N(1)–Ni–N(2)	77.4(1)
OW(1)–Ni–N(1)	94.8(1)		

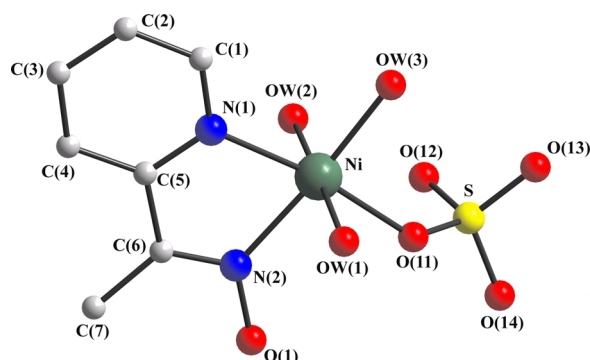


Fig. 4. Ball-and-stick presentation of the molecular structure of $\mathbf{1}$ in $\mathbf{1} \cdot \text{H}_2\text{O}$ and crystallographic numbering scheme adopted (hydrogen atoms omitted for clarity).

The employment of base in the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}/(\text{py})\text{C}(\text{Me})\text{NOH}$ reaction system leads to the isolation of $[\text{Ni}_6(\text{SO}_4)_4(\text{OH})\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3(\text{MeOH})_2(\text{H}_2\text{O})]$ [35]. Of particular note is that the above-mentioned hexanuclear compound is the highest-nuclearity nickel(II) sulfato cluster that has been characterized; the oximate and sulfate ligands adopt the novel 3.211 and 3.2100 (Fig. 3) ligation modes, respectively. The conversion of the mononuclear compound $\mathbf{1} \cdot \text{H}_2\text{O}$ into 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 MeOH at 35–40 °C (eq. (2)).

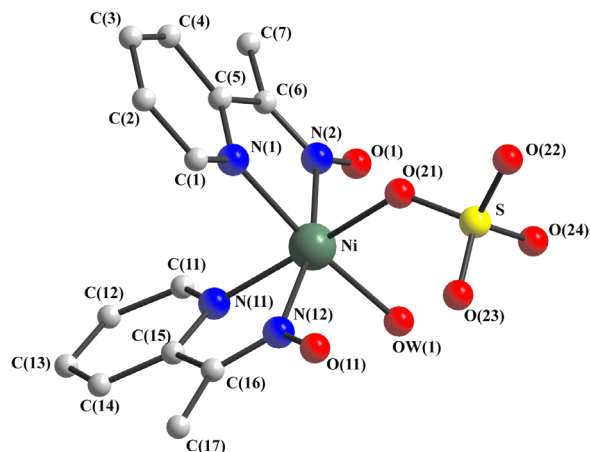
Description of structures

Selected interatomic distances and angles for complexes $\mathbf{1} \cdot \text{H}_2\text{O}$ and $\mathbf{2} \cdot \text{H}_2\text{O}$ are listed in Tables 1 and 3,

D–H...A	D...A	H...A	D–H...A	Sym. operation of A
OW(1)–HA(OW1)···O(14)	2.721	1.902	164.7	$-x, -y+1, -z+1$
OW(1)–HB(OW1)···OW(4) ^b	2.787	1.959	177.1	$x+1, -y+3/2, z+1/2$
OW(2)–HA(OW2)···O(12)	2.689	1.965	168.8	x, y, z
OW(2)–HB(OW2)···O(13)	2.761	1.953	171.9	$-x, -y+1, -z$
OW(3)–HA(OW3)···O(14)	2.751	1.992	168.1	$x+1, y, z$
OW(3)–HB(OW3)···O(12)	2.700	1.898	176.9	$-x, -y+1, -z$
O(1)–H(O1)···OW(4) ^b	2.757	2.018	143.1	$x+1, -y+3/2, z+1/2$
OW(4)–HA(OW4)···O(14)	2.796	2.135	170.7	$x+1, -y+3/2, z-1/2$
OW(4)–HB(OW4)···O(13)	2.820	2.050	167.4	$-x, y+1/2, -z+1/2$

Table 2. Dimensions of the hydrogen bonds (Å, deg) in complex **1** · H₂O.^a

^a A = acceptor, D = donor; ^b atom OW(4), not shown in Fig. 4, belongs to the lattice water molecule.

Fig. 5. Ball-and-stick presentation of the molecular structure of **2** in **2** · H₂O and crystallographic numbering scheme adopted (hydrogen atoms omitted for clarity).

respectively. The molecular structures of the two compounds are shown in Figs. 4 and 5.

Complex **1** · H₂O crystallizes in the monoclinic space group *P*2₁/*n*. Its structure consists of mononuclear complex molecules and hydrate molecules; the latter are not discussed here any further. The Ni^{II} ion is coordinated by one monodentate sulfato ligand, three terminal aqua ligands and one *N,N'*-chelating (py)C(Me)NOH molecule. Thus, adopting the Harris notation [21], (py)C(Me)NOH behaves as an 1.011 ligand (see Fig. 2). The sulfato ligand is *trans* to the pyridyl nitrogen atom (N(1)), while the three aqua ligands are in *mer* positions.

The coordination sphere of the metal center in **1** · H₂O exhibits a slightly distorted octahedral geometry as a consequence of the relatively small bite angle of the chelating ligand (N(1)–Ni–N(2) = 77.4°). The molecule has no imposed symmetry. The Ni–N_{oxime} and Ni–N_{pyridyl} bond lengths of 2.076(2) and 2.072(2) Å, respectively, agree well with values observed for Ni^{II}–N bonds in octahedral complexes [36–39]. The sulfate S–O bond distances do not dis-

Table 3. Selected bond lengths (Å) and angles (°) relevant to the nickel coordination sphere in **2** · H₂O.

Ni–O(21)	2.059(2)	Ni–N(12)	2.066(2)
Ni–OW(1)	2.052(2)	S–O(21)	1.479(2)
Ni–N(1)	2.079(2)	S–O(22)	1.456(2)
Ni–N(2)	2.094(2)	S–O(23)	1.466(2)
Ni–N(11)	2.103(2)	S–O(24)	1.470(2)
O(21)–Ni–OW(1)	88.9(1)	OW(1)–Ni–N(12)	91.4(1)
O(21)–Ni–N(1)	87.6(1)	N(1)–Ni–N(2)	77.0(1)
O(21)–Ni–N(2)	94.2(1)	N(1)–Ni–N(11)	88.2(1)
O(21)–Ni–N(11)	171.8(1)	N(1)–Ni–N(12)	94.7(1)
O(21)–Ni–N(12)	96.5(1)	N(2)–Ni–N(11)	91.7(1)
OW(1)–Ni–N(1)	173.3(1)	N(2)–Ni–N(12)	166.2(1)
OW(1)–Ni–N(2)	97.6(1)	N(11)–Ni–N(12)	76.9(1)
OW(1)–Ni–N(11)	95.9(1)		

play a pattern consistent with its monodentate character. Thus, the S–O(11) bond distance (1.482(2) Å) is very similar to the S–O(12,13,14) distances (average value: 1.477(2) Å) involving the uncoordinated oxygen atoms. This is attributed to the participation of the “free” oxygen atoms in hydrogen bonding interactions.

There is extensive hydrogen bonding in **1** · H₂O (Table 2). The oxime ligand is strongly hydrogen bonded to the O atom of the lattice H₂O molecule. All uncoordinated sulfato O atoms act as acceptors; the donors for these hydrogen bonds are the lattice and coordinated H₂O molecules. The sulfato oxygen atoms participate in three (O(14)) or two (O(12,13)) hydrogen bonds; the lattice water molecule, OW(4), acts both as a donor and as an acceptor. Hydrogen bonds in **1** create 2D networks in layers parallel to the *ac* plane.

Complex **2** · H₂O crystallizes in the monoclinic space group *P*2₁/*n*. Its structure consists of mononuclear complex molecules and hydrate molecules. Two bidentate chelating (py)C(Me)NOH molecules (1.011 [21], see Fig. 2), one monodentate sulfato ligand (1.1000 [21]) and one terminal H₂O molecule create a six-fold coordination at the Ni^{II} ion. Thus, in **1** · H₂O and **2** · H₂O all the ligands adopt the same coordination modes; the difference of the two compounds

D–H...A	D...A	H...A	D–H...A	Sym. operation of A
OW(1)–HA(OW1)...O(24)	2.842	2.106	146.0	$-x, -y+1, -z+1$
OW(1)–HB(OW1)...OW(2) ^b	2.675	1.962	162.4	$-x+1/2, y+1/2, -z+3/2$
O(1)–H(O1)...O(24)	2.603	1.734	171.1	$-x, -y+1, -z+1$
O(11)–H(O11)...O(23)	2.539	1.693	174.8	x, y, z
OW(2)–HA(OW2)...O(22)	2.789	2.086	177.3	$x+1/2, -y+1/2, z+1/2$
OW(2)–HB(OW2)...O(22)	2.793	2.069	151.8	$-x-1/2, y-1/2, -z+3/2$

Table 4. Dimensions of the hydrogen bonds in complex **2** · H₂O.^a^a A = acceptor, D = donor; ^b atom OW(2), not shown in Fig. 5, belongs to the lattice water molecule.Table 5. Formulae, coordination modes of the ligands, and cores of structurally characterized metal complexes of (py)C(Me)NOH and/or (py)C(Me)NO[−].

Complex ^a	Coord. modes ^b	Core ^c	Ref.
[Mn ^{III} ₃ O(O ₂ CMe) ₃ {(py)C(Me)NO} ₃]	2.111	[Mn ^{III} ₃ (μ ₃ -O)] ⁷⁺	[14, 15]
[Mn ^{III} ₃ O(O ₂ CEt) ₃ {(py)C(Me)NO} ₃]	2.111	[Mn ^{III} ₃ (μ ₃ -O)] ⁷⁺	[14, 15]
<i>fac</i> -[Co ^{III} {(py)C(Me)NO} ₃]	1.011		[43]
[NiBr ₂ {(py)C(Me)NOH} ₂]	1.011		[26]
[Ni{(py)C(Me)NO}{(py)C(Me)NOH}(H ₂ O) ₂] ^{+d}	1.011, 1.011		[26, 44]
[Ni ₆ (SO ₄) ₄ (OH){(py)C(Me)NO} ₃ {(py)C(Me)NOH} ₃ (MeOH) ₂ (H ₂ O)]	3.211, 1.011	[Ni ₆ (μ ₃ -OH)(μ ₃ -SO ₄) ₃ (μ ₃ -ONR) ₃] ^{2+e}	[35]
[Ni(SO ₄) ₄ {(py)C(Me)NOH}(H ₂ O) ₃]	1.011		this work
[Ni(SO ₄) ₄ {(py)C(Me)NOH} ₂ (H ₂ O)]	1.011		this work
[ZnCl ₂ {(py)C(Me)NOH} ₂]	1.011		[24]
[Zn ₄ (OH) ₂ Cl ₂ {(py)C(Me)NO} ₄]	2.111	[Zn ₄ (μ-OH) ₂] ⁶⁺	[24]
[Zn(NO ₃) ₂ {(py)C(Me)NOH} ₂]	1.011		[27]
[Rh ^{III} Cl ₂ {(py)C(Me)NO}{(py)C(Me)NOH}]	1.011, 1.011		[45]
[Pt ^{II} {(py)C(Me)NO} ₂]	1.011		[46]
[nBu ₈ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.101	[Sn ^{IV} ₄ (μ ₃ -O) ₂] ¹²⁺	[47]
[Et ₈ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.101	[Sn ^{IV} ₄ (μ ₃ -O) ₂] ¹²⁺	[47]
[Me ₈ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.111	[Sn ^{IV} ₄ (μ ₃ -O) ₂] ¹²⁺	[48]
[Ph ₃ Sb{(py)C(Me)NO} ₂]	1.100		[49]

^a Counterions and lattice solvent molecules have been omitted; ^b using the Harris notation [21]; ^c only for the polynuclear complexes; the nitrogen atoms of the μ₃ 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 [Ni₆(μ₃-OH)(μ-OR')₃(μ-OR'')₃]²⁺, where R' = -SO₃ and R'' = -NC(py)(Me).

is the replacement of two H₂O molecules in **1** · H₂O by one *N,N'*-chelating oxime ligand in **2** · H₂O.

Complex **2** · H₂O is the *cis-cis-trans* isomer considering the positions of the coordinated SO₄^{2−}/H₂O, pyridyl nitrogen and oxime nitrogen atoms, respectively. The *cis* arrangement of the oxime groups appears to be unfavorable, probably due to the steric hindrance arising from the methyl groups upon oxime coordination. The Ni^{II} ion adopts a distorted octahedral geometry. Angular distortions from octahedral geometry are primarily a consequence of the chelating (py)C(Me)NOH ligands and their restricted bite angles (77.0(1), 76.9(1)°). In **2** · H₂O, the Ni–N_{oxime} (average 2.080 Å), Ni–N_{pyridyl} (average 2.091 Å) and Ni–O_{sulfate} (2.059(2) Å) bond lengths are typical [36–39, 40–42].

As in **1** · H₂O, there is also extensive hydrogen bonding in **2** · H₂O (Table 4). Each (py)C(Me)NOH oxime group is strongly hydrogen bonded (intra- or intermolecularly) to uncoordinated O atoms of the sulfato ligand. All uncoordinated O atoms of

the sulfato ligand act as acceptors; the donors for these hydrogen bonds are the lattice/coordinated H₂O molecules and the neutral organic ligands. The sulfato atoms O(22) and O(24) participate in two hydrogen bonds, the lattice water molecule OW(2) acts both as a donor and as an acceptor. The hydrogen bonds create a ladder-type 1D network along the *a* axis (see Fig. 6).

Complexes **1** · H₂O and **2** · H₂O join a small but growing family of structurally characterized metal complexes containing the neutral or anionic forms of methyl(2-pyridyl)ketone oxime as ligands. Since most of these complexes have been reported only recently, we felt it timely to collect the structurally characterized metal complexes of (py)C(Me)NOH and/or (py)C(Me)NO[−] in Table 5, together with the cores of the polynuclear complexes and the ligands' coordination modes for convenient comparison. Inspection of Table 5 shows that the 1.011 ligation mode (Fig. 2) is the exclusive one for the metal complexes containing the neutral ligand.

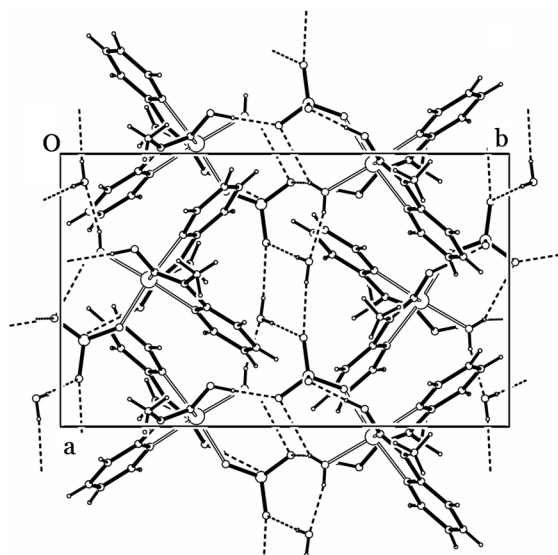
Complexes **1** · H₂O and **2** · H₂O are new members of the rather small family of structurally character-

Table 6. Formulae and coordination modes of the sulfato ligand and for the structurally characterized mononuclear nickel(II) sulfato complexes.

Complex ^a	Coord. mode of the sulfato ligand ^b	Ref.
[Ni(SO ₄)(L)] ^c	1.1100	[41]
[Ni(SO ₄)(phen)(H ₂ O) ₃] ^d	1.1000	[50, 51]
[Ni(SO ₄)(allo) ₂ (H ₂ O) ₃] ^e	1.1000	[52]
[Ni(SO ₄)(L ₁) ₂ (MeOH)] ^f	1.1000	[53]
[Ni(SO ₄)(L ₂) ₂] ^g	1.1000	[54]
[Ni(SO ₄)(L ₃)(H ₂ O)] ^h	1.1000	[55]
[Ni(SO ₄)(L ₄)(H ₂ O) ₂] ⁱ	1.1000	[56]
[Ni(SO ₄)(L ₅)(H ₂ O) ₂] ^j	1.1000	[57]
[Ni(SO ₄)(L ₆)] ^k	1.1100	[58]
[Ni(SO ₄){(py)C(Me)NOH}(H ₂ O) ₃]	1.1000	this work
[Ni(SO ₄){(py)C(Me)NOH} ₂ (H ₂ O)]	1.1000	this work

^a Counterions and lattice solvent molecules have been omitted;

^b using the Harris notation [21]; ^c L = *N,N'*-bis(5-*t*-butyl-3-(piperidinomethyl)salicylidene)-2,2'-biphenylenediamine; ^d phen = 1,10-phenanthroline; ^e allo = allopurinol; ^f L₁ = bis(2,2'-amino-4,4'-bithiazole); ^g L₂ = 1,3-diaminoprop-2-yl β-D-glucopyranoside; ^h L₃ = 6-(4,6-diamino-5-azonia-1,3-diazin-2-yl)-1,4,6,8,11-pentaazacyclotetradecane; ⁱ L₄ = *N*-(3-aminopropyl)-1,3-propanediamine; ^j L₅ = 2,4,6-tri-2-pyridyl-1,3,5-triazine; ^k L₆ = *N,N',N''*-tris(L-rhamnosyl)-tris(2-aminoethyl)amine-*N,N',N''*.

Fig. 6. Projection of the 1D network created by the hydrogen bonds in **2** · H₂O onto the *ab* plane.

ized mononuclear Ni(II) compounds containing the sulfate anion as ligand (see Table 6). With two exceptions (entries 1 and 9 in Table 6), the sulfate ion adopts the 1.1000 ligation mode in these mononuclear Ni(II) complexes. In every case, there is only *one* sulfate ion coordinated to the metal center. In compound [Ni(SO₄)(phen)(H₂O)₃] [50, 51], the coordination sphere of Ni^{II} is similar to that in **1** · H₂O.

Infrared characterization

The IR spectra of **1** · H₂O and **2** · H₂O are similar as expected from the same ligand set present. The complexes exhibit a strong, multi-structured broad band in the 3400–3200 cm^{−1} region, assignable to ν(OH) vibrations indicative of hydrogen bonding [37]. The IR spectrum of the free, *i.e.* ionic, sulfate (the ion belongs to the *T_d* point group) consists of two bands at ~ 1105 and ~ 615 cm^{−1}, assigned to the ν₃(*F₂*) stretching (ν₄(SO)) and ν₄(*F₂*) bending (δ₄(OSO)) modes, respectively [28, 59]. The coordination of SO₄^{2−} to metal ions decreases the symmetry of the group and the ν₃ and ν₄ modes are split [28, 59]. In the case the SO₄^{2−} site symmetry is lowered from *T_d* to *C_{3v}* (monodentate coordination), both ν₁ and ν₂ appear in the IR spectrum with weak to medium intensity, while both ν₃ and ν₄ split into two bands in both the IR and Raman spectra [59]. Complexes **1** · H₂O and **2** · H₂O have *C_{3v}* symmetry at their sulfato ligand. The bands at about 1120 and 1050 cm^{−1} are therefore attributed [59] to the ν₃ modes, while the bands at about 620 and 590 cm^{−1} are assigned [59] to the ν₄ modes. The bands at ~ 980 and ~ 480 cm^{−1} can be assigned to the ν₁ and ν₂ modes, respectively [59].

The medium intensity bands at 1566 and 1116 cm^{−1} in the spectrum of the free ligand (py)C(Me)NOH are assigned to ν(C=N)_{oxime} and ν(N–O)_{oxime}, respectively [60]. The 1116 cm^{−1} band is shifted to a lower wavenumber (1092 cm^{−1}) in **1** · H₂O. This shift is attributed to the coordination of the oxime nitrogen atom [24]. The 1566 cm^{−1} band is shifted to a higher wavenumber (1604 cm^{−1}, overlapping with an aromatic stretch) indicating the oxime nitrogen coordination [24]. Analogous shifts are observed in the spectrum of **2** · H₂O.

The in-plane deformation band of the 2-pyridyl ring of free (py)C(Me)NOH at 632 cm^{−1} shifts upwards (~ 645 cm^{−1}) in the spectra of the complexes, confirming the involvement of the N atom in coordination [61].

Thermal decomposition studies of complexes **1** · H₂O and **2** · H₂O

The thermal decomposition of complexes **1** · H₂O and **2** · H₂O was studied using thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) techniques under nitrogen. TG and DTG data for **1** · H₂O are shown in Fig. 7.

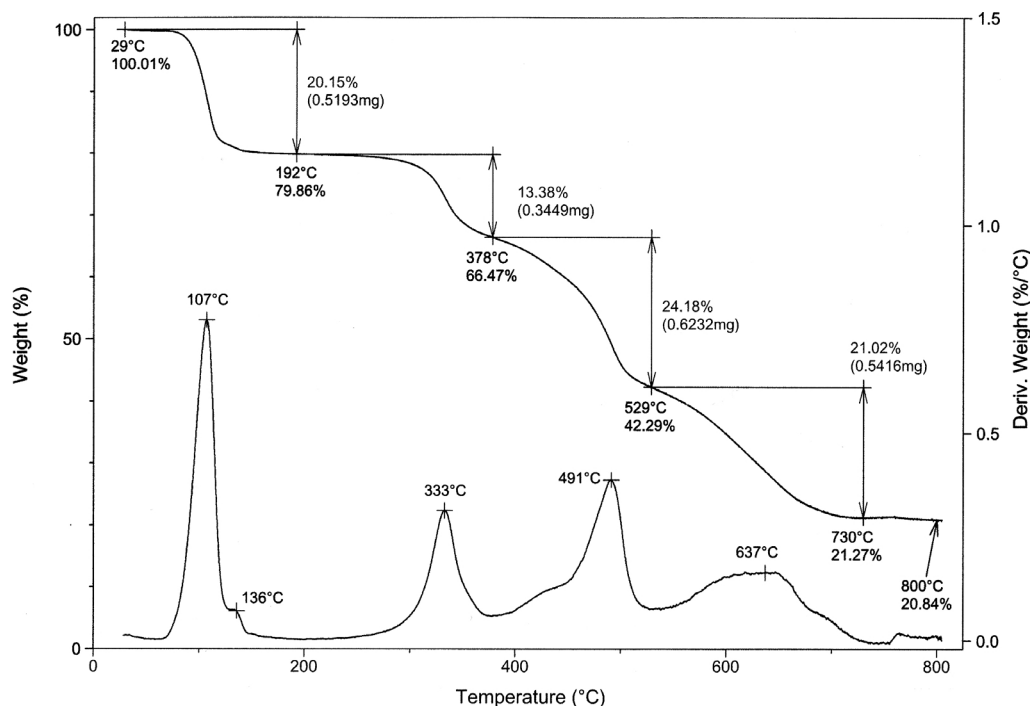


Fig. 7. Thermogravimetric (upper curve) and differential thermogravimetric (lower curve) data for complex **1** · H₂O.

Complex **1** · H₂O decomposes *via* an anhydrous stable intermediate. Between r.t. and ~130 °C an initial, endothermic mass loss of 20.2 % is observed that corresponds satisfactorily to the release of all the water content (calcd.: 19.8 %). A clear plateau is reached at about 135 °C up to ~250 °C, suggesting that the anhydrous species with the empirical formula “Ni(SO₄){(py)C(Me)NOH}” is thermally stable. The IR spectrum of the anhydrous product (obtained after a TG experiment up to 140 °C by keeping the heating rate at 1 °C min⁻¹) is different in the sulfate band region compared to that of **1** · H₂O. This may indicate formation of an anhydrous coordination polymer through sulfato bridges. The anhydrous intermediate decomposes above 260 °C in several steps without the formation of discrete intermediates. An amorphous residue of NiO (found: 20.8; calcd.: 20.5 %) is obtained at ~800 °C.

A similar thermal decomposition behavior is observed for compound **2** · H₂O. There is a mass loss of 7.9 % in two overlapping steps between r.t. and 100 °C that corresponds satisfactorily to the release of all the water content (calcd.: 7.8 %). A clear plateau is reached at about 115 °C up to ~220 °C, suggesting that the anhydrous species with the empirical formula

“Ni(SO₄){(py)C(Me)NOH}₂” is thermally stable. The H₂O-free intermediate may be a mononuclear complex with a chelating (instead of monodentate) sulfato ligand, or a sulfato-bridged coordination polymer. There is a new mass loss of 27.1 % in the range of 230–350 °C indicating the release of one ligand molecule (calcd.: 29.4 %) that is followed immediately by further decomposition without the formation of new intermediates. The final residue at 800 °C appears to be NiO (found: 15.9; calcd.: 16.0 %).

Attempts for the preparation of compounds “Ni(SO₄){(py)C(Me)NOH}” and “Ni(SO₄){(py)C(Me)NOH}₂” from solution have been unsuccessful.

Concluding Comments and Perspectives

The use of the sulfate ligand in combination with *neutral* (py)C(Me)NOH (*i. e.*, in the *absence* of an external base) in aqueous Ni(II) chemistry has provided access to the two new neutral complexes [Ni(SO₄){(py)C(Me)NOH}(H₂O)₃] · H₂O (**1** · H₂O) and [Ni(SO₄){(py)C(Me)NOH}₂(H₂O)] · H₂O (**2** · H₂O). In both complexes the organic ligand chelates through its nitrogen atoms and the sulfate anion behaves as a monodentate ligand. Compounds **1** · H₂O and **2** · H₂O

join a small family of structurally characterized metal complexes containing the neutral or anionic forms of methyl(2-pyridyl)ketone oxime as ligands, while they are new examples of structurally characterized compounds in which (py)C(Me)NOH exists exclusively in its neutral form.

The presence of terminal aqua ligands in **1** · H₂O and **2** · H₂O offers sites for facile incorporation of bidentate organic ligands to obtain high-nuclearity clusters or coordination polymers of Ni^{II}. Analogues of **1** · H₂O and **2** · H₂O with phenyl(2-pyridyl)ketone oxime, (py)C(ph)NOH, are not known to date, and it is currently not evident whether the stability of these species is dependent on the particular nature of the 2-pyridyl oxime ligand. We are studying this matter. Synthetic efforts are also in progress to “activate” the bridging potential of the sulfate ligand in Ni^{II} complexes containing neutral 2-pyridyl oximes as a means to get access to clusters and polymers with interesting structural and magnetic properties.

Experimental Section

All manipulations were performed under aerobic conditions using materials and solvents (Merck, Aldrich) as received. Methyl(2-pyridyl)ketone oxime, (py)C(Me)NOH, was synthesized by the reaction of equimolar quantities of 1-pyridin-2-yl-ethanone (2-acetylpyridine), (py)C(Me)O, H₂NOH · HCl and NaOEt in EtOH [62]. Elemental analyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. IR spectra (4000–400 cm^{−1}) were recorded on a Perkin-Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) experiments were performed on the SDT-2960 module from TA-instruments in a dinitrogen gas flow; sample weights of 5–15 mg and heating rates of 1 and 5 °C min^{−1} were used.

[Ni(SO₄){(py)C(Me)NOH}(H₂O)₃] · H₂O (**1** · H₂O)

A green solution of NiSO₄ · 6 H₂O (0.263 g, 1.00 mmol) in H₂O (10 mL) was added to a stirred slurry of (py)C(Me)NOH (0.136 g, 1.00 mmol) in H₂O (15 mL). The resulting green solution was stirred for about 1 h at r. t. A small quantity of undissolved material was removed by filtration and the green filtrate layered with Me₂CO (50 mL). Slow mixing gave X-ray quality light blue-green crystals of the product. The crystals were collected by filtration, washed with cold H₂O (1 mL) and ice-cold Me₂CO (2 × 3 mL), and dried in air. Typical yields were in the 60–70 % range. – IR (KBr pellet): ν = 3440, 3180, 2714, 2362, 2336, 1604,

Table 7. Summary of crystal data, data collection and structure refinement for the X-ray diffraction study of complexes **1** · H₂O and **2** · H₂O.

Complex	1 · H ₂ O	2 · H ₂ O
Chemical formula	C ₇ H ₁₆ NiN ₂ O ₉ S	C ₁₄ H ₂₀ NiN ₄ O ₈ S
Formula weight	362.99	463.11
Colour, habit	light blue prisms	blue-purple prisms
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	7.088(3)	9.982(3)
<i>b</i> , Å	21.871(9)	16.421(4)
<i>c</i> , Å	9.283(3)	11.914(3)
β , deg	104.00(1)	93.15(1)
<i>V</i> , Å ³	1396.4(9)	1949.9(9)
<i>Z</i>	4	4
<i>D</i> _{calc} , g cm ^{−3}	1.727	1.578
Temperature, K	298	298
μ (MoK α), mm ^{−1}	1.582	1.152
<i>F</i> (000), e	752	960
Scan mode/speed, deg min ^{−1}	θ -2 θ /5	θ -2 θ /2.5
θ Range, deg	1.86–24.99	2.39–25.00
Ranges <i>hkl</i>	+8, +26, −9 – +10	+11, +19, +14
Measured reflections	2228	3596
Unique reflections/ <i>R</i> _{int}	2062/0.011	3426/0.011
Reflections with <i>I</i> ≥ 2 σ (<i>I</i>)	1932	2917
Parameters refined	234	333
GoF (on <i>F</i> ²)	1.076	1.067
<i>R</i> 1 ^a [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.033	0.029
<i>wR</i> 2 ^b [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.093	0.073
$\Delta\rho_{\max}/\min$, e Å ^{−3}	0.58/−0.81	0.29/−0.35

^a $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; ^b $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$.

1488, 1382, 1336, 1262, 1120, 1092, 1048, 981, 912, 849, 782, 754, 644, 618, 592, 476, 428 cm^{−1}. – C₇H₁₆NiN₂O₉S (362.99): calcd. C 23.16, H 4.44, N 7.72; found C 23.32, H 4.23, N 7.59.

[Ni(SO₄){(py)C(Me)NOH}₂(H₂O)] · H₂O (**2** · H₂O)

A green solution of NiSO₄ · 6 H₂O (0.263 g, 1.00 mmol) in H₂O (10 mL) was added to a stirred slurry of (py)C(Me)NOH (0.408 g, 3.00 mmol) in H₂O (15 mL). A noticeable color change from green to red-orange occurred. The resulting red-orange solution was stirred for about 1 h at r. t. A small quantity of undissolved material was removed by filtration and the filtrate layered with Me₂CO (50 mL). Slow mixing gave X-ray quality blue-purple crystals of the product. The crystals were collected by filtration, washed with cold H₂O (1 mL) and ice-cold Me₂CO (2 × 3 mL), and dried in air. Typical yields were in the 55–65 % range (based on Ni^{II}). – IR (KBr pellet): ν = 3488, 3400, 3084, 3026, 2930, 1638, 1598, 1480, 1442, 1378, 1330, 1258, 1126, 1092, 1046, 984, 892, 788, 748, 684, 645, 624, 590, 486, 424 cm^{−1}. – C₁₄H₂₀NiN₄O₈S (463.11): calcd. C 36.31, H 4.35, N 12.10; found C 36.18, H 4.42, N 12.23.

Crystal structure determination

Light blue prismatic crystals of **1**·H₂O (0.15 × 0.20 × 0.50 mm) and blue-purple prismatic crystals of **2**·H₂O (0.10 × 0.30 × 0.50 mm) were mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated MoK α radiation (λ = 0.71073 Å). Crystal data and full details of the data collection and data processing are listed in Table 7. Unit cell dimensions were refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23^\circ$. Three standard reflections monitored every 97 reflections showed less than 3 % variation and no decay. Lorentz, polarization and Ψ scan absorption corrections were applied using Crystal Logic software.

The structures were solved by Direct Methods using SHELXS-86 [63] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [64]. All hydrogen atoms

were located by difference maps and were refined isotropically, except those of the methyl group for complex **1**·H₂O, which were introduced at calculated positions as riding on bonded atoms. For both structures all non-hydrogen atoms were refined using anisotropic displacement parameters.

CCDC 640683 (**1**·H₂O) and 640684 (**2**·H₂O) 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.

Acknowledgement

S. P. P., E. M.-Z., C. P. and C. P. R. thank the European Social Fund (ESF), the Operational Program for Educational and Vocational Training II (EPEAEK II) and particularly the Program PYTHAGORAS (Grant b. 365.037) for funding the above work.

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