

Investigation of the Zinc Chloride / Methyl(2-pyridyl)ketone Oxime Reaction System: A Mononuclear Complex and an Inverse 12-Metallacrown-4 Cluster

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This paper is dedicated to the memory of Dimitris Katakis, Professor of Inorganic Chemistry in the Chemistry Department of the University of Athens

The reactions of methyl(2-pyridyl)ketone oxime, (py)C(Me)NOH, with zinc chloride have been investigated. An excess of the ligand in EtOH/MeCN affords the mononuclear complex $[\text{ZnCl}_2\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_2]$ (**1**) in moderate yield. The metal ion is coordinated by two chloro ligands and two *N,N'*-chelating (py)C(Me)NOH molecules. The six-coordinate molecule is the *cis-cis-trans* isomer considering the positions of the coordinated chlorine, pyridyl and oxime nitrogen atoms, respectively. The reaction between equimolar quantities of ZnCl_2 , (py)C(Me)NOH and $\text{LiOH} \cdot \text{H}_2\text{O}$ in EtOH/MeCN leads to the tetranuclear cluster $[\text{Zn}_4(\text{OH})_2\text{Cl}_2\{(\text{py})\text{C}(\text{Me})\text{NO}\}_4]$ (**2**) in high yield. The molecule lies on a crystallographic inversion center and has an inverse 12-metallacrown-4 topology. Two triply bridging hydroxides are accommodated within the metallacrown ring. Each (py)C(Me)NO[−] ligand adopts the 2.111 coordination mode (Harris notation), chelating one Zn^{II} ion and bridging a Zn^{II}_2 pair. Two metal ions are in a distorted O_2N_4 octahedral environment, whereas the other two are in a severely distorted tetrahedral O_3Cl environment. Complex **2** joins a small family of structurally characterized zinc(II) metallacrown complexes. 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, Inverse 12-Metallacrown Complexes, Methyl(2-pyridyl)ketone Oxime Complexes, Zinc(II) Chloro Complexes

Introduction

The study of metallamacrocycles has been intensified over the last 15 years due to the fact that this class of compounds is relevant to a variety of modern chemical interests [1], including catalysis [2], sensors [3], molecular recognition [4] and chiral building blocks for 1D, 2D and 3D solids [5]. Metallamacrocycles include complexes such as metallacrowns [6], metallahelicates [7], molecular squares and boxes [8,9], metallacalixarenes [10], and metallacryptates and metallacryptands [1, 11].

Metallacrowns (MCs) [6] were first described by Pecoraro's group [12] sixteen years ago. MCs, the inorganic structural and functional analogues of crown ethers [13], are usually formed with a transition metal ion and a nitrogen donor ligand replacing the meth-

ylene carbon atoms. The original MC structures described contain a $-\text{[M-N-O]}_n-$ repeat unit, where $n = 3, 4$ and 5 [6]. The nomenclature for metallacrowns is derived from that of crown ethers and has been discussed in detail [6]. It should be mentioned at this point that some researchers prefer to consider MCs simply as one sub-area of metal wheel (ring) chemistry, avoiding the use of their specialized nomenclature. These metallamacrocycles are now quite diverse and include expanded metallacrowns (carbon atoms are included in the repeat unit) [14], metallacoronates (both of the heteroatoms are oxygen atoms with carbon atom extenders) [15], azametallacrowns (the oxygen atoms replaced by nitrogen atoms to give a $-\text{[M-N-N]}-$ repeat unit) [16] and expanded azametallacrowns (carbon atoms are included in the repeat unit) [17]. Now diverse MCs with varying ring

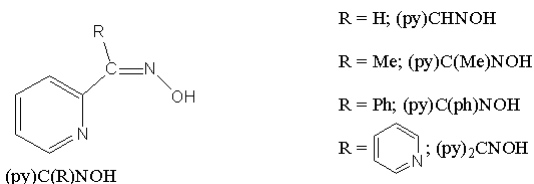


Fig. 1. General structure and abbreviations of simple 2-pyridyl oximes, including methyl 2-pyridyl ketone oxime [(py)C(Me)NOH].

sizes are known [1, 6], including 9-MC-3, 12-MC-3, 12-MC-4, 12-MC-6, 15-MC-5, 15-MC-6, 16-MC-4, 16-MC-8, 18-MC-6, 22-MC-8, 24-MC-6, 24-MC-8, 30-MC-10 and 36-MC-12. Metallacrowns (in their broad sense) have been studied for their selective cation and anion binding [6, 18], ability to stabilize active molecules [19], as sensors [3], as antibacterial compounds [20], as building blocks for extended solids [5], and as single-molecule magnets [1].

Restricting further discussion to classical MCs, *i. e.* those containing the $-[M-N-O]_n-$ repeat unit, it is known that their synthesis requires the employment of tri- and tetradentate ligands containing hydroxamate or oximate functionalities to provide a scaffolding within which the desired metal-containing core can be realized. Very popular ligands for the construction of MCs are 2-pyridyl ketone oximes [(py)C(R)NOH, Fig. 1] in their anionic form [6, 21–29].

We have been exploring the chemistry of MCs [28, 29] and the coordination chemistry of 2-pyridyl oximes [(py)C(R)NOH, Fig. 1] [28–34], the latter not necessarily in relation to the former. There is currently a renewed interest in the coordination chemistry of 2-pyridyl oximes [35, 36]. The anionic forms of these molecules are versatile ligands for a variety of objectives, including μ_2 and μ_3 behaviour, formation of polynuclear metal complexes (clusters), isolation of coordination polymers, mixed-metal chemistry and significant magnetic properties; the activation of 2-pyridyl oximes by 3d-metal centers towards further reactions is also becoming a fruitful area of research. 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 [35, 36].

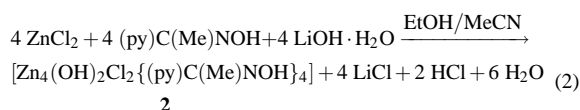
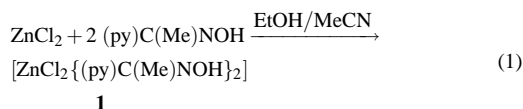
Zinc(II) metallacrown complexes based on 2-pyridyloximate ligands have attracted some prior interest [21, 25, 28, 37]; details will be given in “Results and Discussion”. Seeking to extend the family of Zn(II) MCs incorporating new 2-pyridyloximate lig-

ands and to examine the possibility of creating novel cluster topologies within this chemistry, we report here studies of the reactions of methyl 2-pyridyl ketone oxime [(py)C(Me)NOH, Fig. 1] with $ZnCl_2$, which have demonstrated that the anionic form of the ligand can give MCs. One synthetically relevant, mononuclear zinc(II) complex is reported.

Results and Discussion

Brief synthetic comments

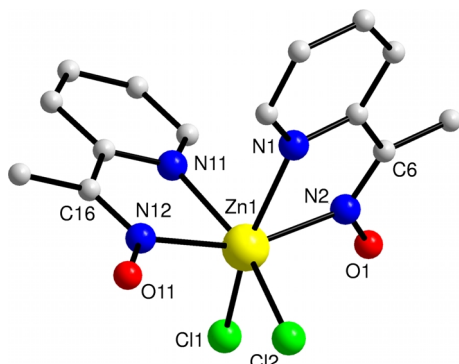
The chemical and structural identities of the products from the $ZnCl_2$ /(py)C(Me)NOH reaction system depend on the OH^- concentration. The mononuclear complex $[ZnCl_2\{(py)C(Me)NOH\}_2]$ (**1**) was isolated from the direct reaction between $ZnCl_2$ and (py)C(Me)NOH, whereas employment of hydroxides lead to the tetranuclear cluster $[Zn_4(OH)_2\{(py)C(Me)NO\}_4]$ (**2**). The preparation of the two complexes is summarized in the balanced eqs (1) and (2):



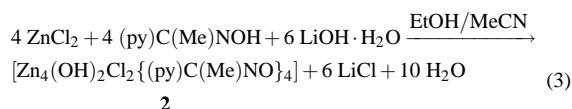
Some features of the reactions represented by eq. (1) and eq. (2) deserve comments. First, the “wrong” $ZnCl_2$ to (py)C(Me)NOH reaction ratio (1:1) employed for the preparation of **1** (see Experimental Section), compared to that required by eq. (1) [1:2], did not prove detrimental to the formation of the complex. With the identity of **1** established by single-crystal X-ray crystallography, the “correct” stoichiometry was employed and led to the pure compound in high yield. Second, the addition of a base is absolutely necessary for the preparation of **2**, which contains the deprotonated ligand, due to the high pK_a value (10.87) of the oxime group of (py)C(Me)NOH [36]. Note that Et_3N can also act as a base to facilitate formation of the deprotonated ligand (the relevant procedure is not mentioned in the Experimental Section). Third, the reaction mixture which leads to **2** should be filtered before crystallization to remove LiCl which is insoluble in EtOH/MeCN; filtration is not necessary if Et_3N is employed as a base. The product also needs to be

Table 1. Selected bond lengths (Å) and angles (°) relevant to the zinc coordination sphere for complex **1**.

Zn(1)–Cl(1)	2.448(1)	Zn(1)–N(2)	2.131(2)
Zn(1)–Cl(2)	2.369(1)	Zn(1)–N(11)	2.213(2)
Zn(1)–N(1)	2.276(2)	Zn(1)–N(12)	2.154(2)
Cl(1)–Zn(1)–Cl(2)	97.4(1)	Cl(2)–Zn(1)–N(12)	88.7(1)
Cl(1)–Zn(1)–N(1)	158.3(1)	N(1)–Zn(1)–N(2)	71.8(1)
Cl(1)–Zn(1)–N(2)	87.6(1)	N(1)–Zn(1)–N(11)	86.8(1)
Cl(1)–Zn(1)–N(11)	87.4(1)	N(1)–Zn(1)–N(12)	90.1(1)
Cl(1)–Zn(1)–N(12)	108.1(1)	N(2)–Zn(1)–N(11)	92.0(1)
Cl(2)–Zn(1)–N(1)	94.7(1)	N(2)–Zn(1)–N(12)	157.3(1)
Cl(2)–Zn(1)–N(2)	105.8(1)	N(11)–Zn(1)–N(12)	73.0(1)
Cl(2)–Zn(1)–N(11)	161.7(1)		

Fig. 2. Partially labelled plot of the molecular structure of complex **1**.

washed with a small amount of H₂O to ensure complete removal of LiCl. Fourth, the simultaneous presence of a hydroxo cluster and HCl in the products of the reaction represented by eq. (2) could suggest that the latter can decompose the former. The high yield (60–70%) of the preparation of **2** is against such a hypothesis. The yield of **2** is not increased employing a ZnCl₂ : (py)C(Me)NOH : LiOH · H₂O ratio of 4:4:6, see eq. (3):



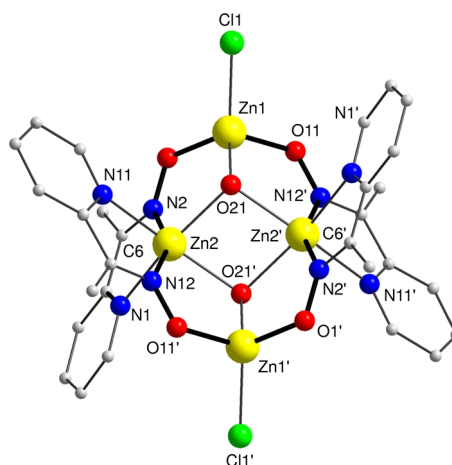
And fifth, complexes **1** and **2** seem to be the only products from the ZnCl₂/(py)C(Me)NOH reaction system. The ZnCl₂ : (py)C(Me)NOH ratio, the nature of the solvent (the solvents MeOH, and MeOH/MeCN were also used), the addition of counter anions such as ClO₄[−] and PF₆[−] (for the isolation of potentially existing cationic complexes) and the crystallization method have no influence on the identity of the products.

The fact that complexes **1** and **2** contain basically the same ligand set (the major difference being the pro-

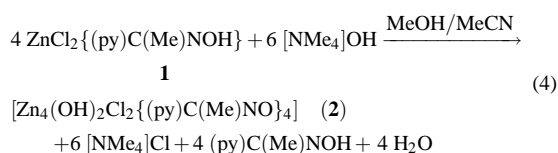
Table 2. Selected bond lengths (Å) and angles (°) relevant to the zinc coordination spheres in complex **2** · 2 Et₂O^a.

Zn(1)···Zn(1')	5.782(4)	Zn(1)–O(21)	1.982(4)
Zn(1)···Zn(2)	3.307(4)	Zn(2)–O(21)	2.105(4)
Zn(1)···Zn(2')	3.327(4)	Zn(2)–O(21')	2.134(4)
Zn(2)···Zn(2')	3.252(4)	Zn(2)–N(1)	2.193(5)
Zn(1)–Cl(1)	2.208(2)	Zn(2)–N(2)	2.113(5)
Zn(1)–O(1)	1.946(5)	Zn(2)–N(11)	2.214(6)
Zn(1)–O(11)	1.960(4)	Zn(2)–N(12)	2.109(5)
Zn(1)–O(21)–Zn(2)	108.0(2)	O(21)–Zn(2)–N(11)	95.0(2)
Zn(1)–O(21)–Zn(2')	107.8(2)	O(21)–Zn(2)–N(12)	107.3(2)
Zn(2)–O(21)–Zn(2')	100.2(2)	O(21')–Zn(2)–N(1)	90.7(2)
Cl(1)–Zn(1)–O(1)	114.5(2)	O(21')–Zn(2)–N(2)	106.9(2)
Cl(1)–Zn(1)–O(11)	106.4(2)	O(21')–Zn(2)–N(11)	162.3(2)
Cl(1)–Zn(1)–O(21)	122.6(1)	O(21')–Zn(2)–N(12)	91.0(2)
O(1)–Zn(1)–O(11)	106.2(2)	N(1)–Zn(2)–N(2)	74.8(2)
O(1)–Zn(1)–O(21)	102.5(2)	N(1)–Zn(2)–N(11)	99.2(2)
O(11)–Zn(1)–O(21)	103.1(2)	N(1)–Zn(2)–N(12)	91.1(2)
O(21)–Zn(2)–O(21')	79.8(2)	N(2)–Zn(2)–N(11)	89.9(2)
O(21)–Zn(2)–N(1)	159.3(2)	N(2)–Zn(2)–N(12)	157.0(2)
O(21)–Zn(2)–N(2)	90.3(2)	N(11)–Zn(2)–N(12)	74.3(2)

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

Fig. 3. Partially labelled ball-and-stick presentation of the tetranuclear molecule of **2** · 2 Et₂O. Primed and unprimed atoms are related by the crystallographic inversion center. O(21) and O(21') are the hydroxo oxygen atoms. The inverse metallacrown ring is highlighted.

tonation state of the ligand), led us to suspect that **1** could be transformed into **2**; this has, indeed, turned out to be the case. Treatment of **1** with [NMe₄]OH in MeOH/MeCN leads to the high-yield (> 70%) isolation of pure **2**. The identity of the product from this transformation was confirmed by microanalysis and IR spectroscopy comparing the results with those for the authentic sample prepared by the method reported in the Experimental Section and represented by eq. (2). The Brönsted acidity of **1** is summarized in eq. (4):



Description of structures

Selected interatomic distances and angles for complexes **1** and **2** · 2 Et₂O are listed in Tables 1 and 2, respectively. The molecular structures of the two complexes are shown in Figs 2 and 3.

Complex **1** crystallizes in the monoclinic space group *P*2₁/*n*. Its structure consists of well-separated [ZnCl₂{(py)C(Me)NOH}₂] molecules. The Zn^{II} ion is coordinated by two chloro ligands and two *N,N'*-chelating (py)C(Me)NOH molecules. The ligating atoms of (py)C(Me)NOH are the nitrogen atoms of the neutral oxime and the 2-pyridyl groups. Thus, adopting the Harris notation [38], (py)C(Me)NOH behaves as an 1.011 ligand, see Fig. 4. The Harris notation describes the binding mode as X.Y₁Y₂Y₃...Y_n, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms (ions) attached to the different donor atoms. The ordering of Y is listed by Cahn-Ingold-Prelog priority rules, hence here O before N.

The six-coordinate molecule is the *cis-cis-trans* isomer considering the positions of the coordinated chlorine, pyridyl nitrogen and oxime nitrogen atoms, respectively. The *cis* arrangement of the oxime groups seems unfavourable, most probably due to the steric hindrance arising from the methyl group upon oxime coordination. The molecule has no imposed symmetry, although it approximates closely *C*₂ symmetry, with the *C*₂ axis bisecting the Cl(1)-Zn(1)-Cl(2) angle. The two Zn-Cl bond lengths [2.448(1), 2.369(1) Å] are rather similar, while the Zn-N_{oxime} bonds [Zn-N = 2.131(2), 2.154(2) Å] are slightly stronger than the Zn-N_{pyridyl} bonds [Zn-N = 2.276(2), 2.213(2) Å]. The Zn-Cl, Zn-N_{oxime} and Zn-N_{pyridyl} bond lengths in **1** compare well with the corresponding distances in other structurally characterized six-coordinate zinc(II) complexes containing terminal chloro ligands [39, 40], pyridyl nitrogen [28, 39–41] or oxime nitrogen atoms [28, 41]. The distortion from perfect octahedral geometry is a consequence of the relatively small bite angle of the chelating ligand [N(1)-Zn(1)-N(2) = 71.8(1), N(11)-Zn(1)-N(12) = 73.0°].

There are two intramolecular hydrogen bonds with the uncoordinated oxime oxygen atoms as donors and the chloro ligands as acceptors. Their dimensions are O(1)...Cl(1) 3.009 Å, H(O1)-Cl(1) 2.246 Å, O(1)-H(O1)...Cl(1) 155.5° and O(11)...Cl(2) 3.114 Å, H(O11)...Cl(2) 2.391 Å, O(11)-H(O11)...Cl(2) 148.6°.

Compound **1** is the *second* structurally characterized zinc(II) complex of (py)C(Me)NOH, see Table 3. The first one was [Zn(NO₃)₂{(py)C(Me)NOH}₂] [41]. The molecular structures of the two complexes are very similar, the only essential difference being the replacement of the terminal chlorides of the former by monodentate nitrate ligands in the latter; an analogous *cis-cis-trans* arrangement has also been observed in the structure of the nitrate complex.

Somewhat to our surprise, complex **1** is only just the third member of a small family that comprises mononuclear, six-coordinate [ZnCl₂(L-L)₂] complexes with a *cis-cis-trans* arrangement of donor atoms, where L-L is an asymmetric *N,N'*-chelating ligand [40, 42].

The tetranuclear molecule of **2** · 2 Et₂O lies on a crystallographic inversion center and has a planar, nearly rhombic arrangement of the metal centers. The two diagonals of the rhombus correspond to the interatomic distances Zn(1)...Zn(1') and Zn(2)...Zn(2') which are equal to 5.782(4) and 3.252(4) Å, respectively, the short diagonal being similar to the sides of the rhombus [3.307(4), 3.327(4) Å]. Due to the presence of the crystallographic inversion center, the {Zn(2)O(21)Zn(2')O(21')}²⁺ sub-core is strictly planar. Using metallacrown nomenclature [6], the formula of the cluster is {(OH)[inv12-MC_{ZnN}{(py)C(Me)NO}-4]Cl₂} · 2 Et₂O. The metallacrown is characterized as *inverse* because the Zn atoms, rather than the oximate oxygen atoms, are oriented towards the center of the cavity. For 12-MC-4 complexes, two structural motifs have been reported: regular [6, 23] and inverse [6, 21, 25, 28, 29, 37], with most 12-MC-4 compounds belonging to the former type. In the regular motif, there is an -N-O-M-N-O-M- linkage, *i. e.*, an -[M-N-O]_n- repeat unit, with the oxygen atoms oriented towards the center of the cavity and capable of binding cations [6]. In the inverse motif, which has been realized only for Zn [21, 25, 28, 37] and Co [29], the ring metal cations, rather than the anionic oxygen atoms, are oriented towards the center of the cavity which is now capable of encapsulating anions, with the connectivity transposed to -N-O-M-O-N-M-.

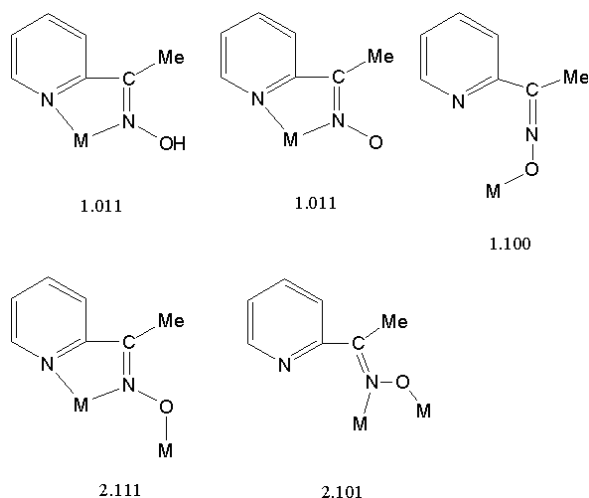


Fig. 4. The crystallographically established coordination modes of (py)C(Me)NOH and (py)C(Me)NO[−] in the hitherto structurally characterized metal complexes.

The Zn centers in **2** · 2 Et₂O are bridged along each side of the rhombus by one μ_3 -hydroxide [O(21), O(21')] and one oximate (−1) group. The (py)C(Me)NO[−] ligands adopt the 2.111 [38] coordination mode. The coordination about the hydroxo oxygen atom, O(21), is markedly pyramidal [sum of Zn–O(21)–Zn angles = 316.0(2)°].

The Zn^{II} ions exhibit two coordination geometries. Zn(2) and Zn(2') are in a distorted *cis-cis-trans* (O_{hydroxo})₂(N_{pyridyl})₂(N_{oximate})₂ octahedral environment, whereas Zn(1) and Zn(1') are in a severely distorted (O_{hydroxo})(O_{oximate})₂Cl tetrahedral environment. Each hydroxo oxygen atom bridges two octahedral Zn^{II} ions and one tetrahedral Zn^{II} ion. The octahedrally coordinated metal ions are bound to two (py)C(Me)NO[−] moieties forming two five-membered chelate rings. The two μ_3 -hydroxide ions are accommodated in the center of the MC ring. The ligands form a propeller configuration that imposes absolute stereoisomerism, with Λ chirality at Zn(2) and Δ chirality at Zn(2'). The longer Zn(2)–O(21, 21') bonds [2.105(4), 2.134(4) Å] compared to the Zn(1)–O(21) one [1.982(4) Å] are a consequence of the higher coordination number of Zn(2). The Zn(1)–Cl(1) bond length [2.208 Å] in **2** · 2 Et₂O is typical for such a terminal bond in tetrahedral zinc(II) complexes [25, 37].

The crystal structure of **2** · 2 Et₂O is stabilized by one crystallographically independent, intermolecular hydrogen bond with the hydroxo oxygen atom [O(21) and its symmetry-related partner O(21')] as donor and

Table 3. Selected structural parameters for the inverse 12-MC-4 complexes [Zn₄(OH)₂Cl₂{(py)₂CNO}₄]^a and **2**.

Parameter [Å] or [°]	[Zn ₄ (OH) ₂ Cl ₂ {(py) ₂ CNO} ₄]	2 · 2 Et ₂ O
Zn _{tetr} ...Zn _{tetr}	5.826	5.782
Zn _{oct} ...Zn _{oct}	3.231	3.252
Zn _{tetr} ...Zn _{oct} ^b	3.326	3.317
Zn _{tetr} ...Cl	2.207	2.208
Zn _{tetr} ...O _{hydroxo}	1.963	1.982
Zn _{tetr} ...O _{oximate} ^b	1.960	1.953
Zn _{oct} ...O _{hydroxo} ^b	2.118	2.120
Zn _{oct} ...N _{pyridyl} ^b	2.178	2.204
Zn _{oct} ...N _{oximate} ^b	2.144	2.111
Zn _{tetr} –O _{hydroxo} –Zn _{oct} ^b	109.4	107.9
Zn _{oct} –O _{hydroxo} –Zn _{oct}	99.4	100.2
Σ(Zn–O _{hydroxo} –Zn)	318.1	316.0

^a The anion (py)₂CNO[−] behaves as a 2.1110 ligand in this complex, i. e., one of the 2-pyridyl rings remains uncoordinated; ^b mean values; oct = octahedral Zn^{II} ion; tetr = tetrahedral Zn^{II} ion.

the diethylether oxygen atom [O(31) and its symmetry-related partner O(31')] as acceptor. Its dimensions are O(21)...O(31) 2.903 Å, H(O21)...O(31) 2.020 Å and O(21)–H(O21)...O(31) 172.6°.

The molecular structure of **2** · 2 Et₂O is very similar to the structures of [Zn₄(OH)₂Cl₂{(py)₂CNO}₄] [25] and [Zn₄(OH)₂Cl₂{(py)CHNO}₄] [37]. Rather than discuss similarities, we list in Table 3 typical structural parameters for the representative complex [Zn₄(OH)₂Cl₂{(py)₂CNO}₄] [25] and for **2** · 2 Et₂O. The remarkable similarity of the molecular structures is clearly evident. Obviously, the replacement of (py)C(Me)NO[−] by (py)CHNO[−] and (py)₂CNO[−] has little structural effect.

Complex **2** · 2 Et₂O extends to ten the number of structurally characterized zinc(II) metallacrown complexes that are based on 2-pyridyloximate ligands. These complexes are summarized in Table 4. The complexes belong to two families. The first family consists of complexes [Zn₄(OH)₂X₂{(py)C(R)NOH}₄], where X[−] is a monodentate (Cl[−] [25, 37], N₃[−] [28], NCO[−] [28]), asymmetric bidentate (MeCO₂[−] [21], PhCO₂[−] [28]) or a bidentate (acac[−] [28]) terminal ligand. These complexes have similar structures with an inverse 12-MC-4 topology. The second family consists of two pentanuclear cationic complexes [28] in which the five Zn^{II} are held together by six (py)₂CNO[−] ligands that adopt three different coordination modes; the chloro and isothiocyanato ligands are terminal. The five Zn^{II} ions define two nearly equilateral triangles sharing a common apex, and the novel Zn₅ topology can be described as two “collapsed” 9-MC-3 motifs sharing a common metal apex. Such structures can not be adopted by using (py)CHNO[−] or

Complex ^a	Topology	Ref.
[Zn ₄ (OH) ₂ Cl ₂ {(py)CHNO} ₄]	inv 12-MC-4	[37]
[Zn ₄ (OH) ₂ Cl ₂ {(py)C(Me)NO} ₄]	inv 12-MC-4	this work
[Zn ₄ (OH) ₂ Cl ₂ {(py) ₂ CNO} ₄]	inv 12-MC-4	[25]
[Zn ₄ (OH) ₂ (O ₂ CMe) ₂ {(py) ₂ CNO} ₄] ^b	inv 12-MC-4	[21]
[Zn ₄ (OH) ₂ (O ₂ CPh) ₂ {(py) ₂ CNO} ₄] ^b	inv 12-MC-4	[28]
[Zn ₄ (OH) ₂ (N ₃) ₂ {(py) ₂ CNO} ₄]	inv 12-MC-4	[28]
[Zn ₄ (OH) ₂ (NCO) ₂ {(py) ₂ CNO} ₄]	inv 12-MC-4	[28]
[Zn ₄ (OH) ₂ (acac) ₂ {(py) ₂ CNO} ₄] ^b	inv 12-MC-4	[28]
[Zn ₅ Cl ₂ {(py) ₂ CNO} ₆][ZnCl(NCS) ₃]	two “collapsed” 9-MC-3 ^c	[28]
[Zn ₅ (NCS) ₂ {(py) ₂ CNO} ₆ (MeOH)][Zn(NCS) ₄]	two “collapsed” 9-MC-3 ^c	[28]

Table 4. Structurally characterized zinc(II) metallacrown complexes based on 2-pyridyloximate ligands.

^a Solvate molecules have been omitted; ^b There are two 5-coordinate Zn^{II} ions instead of two tetrahedrally coordinated Zn^{II} ions; ^c The two “collapsed” 9-MC-3 structures share a common Zn apex; acac[−] = acetylacetonato ligand; inv 12-MC-4 = inverse 12-metallacrown-4.

Table 5. Structurally characterized metal complexes containing (py)C(Me)NOH and/or (py)C(Me)NO[−] as ligands.

Complex ^a	Coordination mode(s)	Coordination spheres; coordination geometries	Ref.
[NiBr ₂ {(py)C(Me)NOH} ₂]	1.011	<i>cis, cis, trans</i> -Ni ^{II} Br ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	[43]
[Zn(NO ₃) ₂ {(py)C(Me)NOH} ₂]	1.011	<i>cis, cis, trans</i> -Zn ^{II} (O _{nitr}) ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	[41]
[ZnCl ₂ {(py)C(Me)NOH} ₂]	1.011	<i>cis, cis, trans</i> -Zn ^{II} Cl ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	this work
[Ni{(py)C(Me)NO} ₂]{(py)C(Me)NOH}(H ₂ O) ₂ (NO ₃)	1.011; 1.011	<i>trans, cis, cis</i> -Ni ^{II} O ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	[43]
[Ni{(py)C(Me)NO} ₂]{(py)C(Me)NOH}(H ₂ O) ₂ (ClO ₄)	1.011; 1.011	<i>trans, cis, cis</i> -Ni ^{II} O ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	[44]
[RhCl ₂ {(py)C(Me)NO} ₂]{(py)C(Me)NOH}	1.011; 1.011	<i>trans, cis, cis</i> -Rh ^{III} Cl ₂ (N _{py}) ₂ (N _{ox}) ₂ ; oct	[45]
[Co{(py)C(Me)NO} ₃]	1.011	<i>fac</i> -Co ^{III} N ₆ ; oct	[31]
[Pt{(py)C(Me)NO} ₂]	1.011	<i>trans</i> -Pt ^{III} N ₄ ; sp	[46]
[Ph ₃ Sb{(py)C(Me)NO} ₂]	1.100	<i>cis, trans</i> -Sb ^V C ₃ (O _{ox}) ₂ ; tbp	[47]
[Bu ⁿ ₄ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.101	Sn ^{IV} C ₂ (μ ₃ -O)(O _{ox})(N _{ox}), Sn ^{IV} C ₂ (μ ₃ -O) ₂ (O _{ox}); spy, tbp	[48]
[Et ₈ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.101	Sn ^{IV} C ₂ (μ ₃ -O)(O _{ox}) ₂ , Sn ^{IV} C ₂ (μ ₃ -O) ₂ (N _{ox}); tbp, spy	[48]
[Me ₈ Sn ₄ O ₂ {(py)C(Me)NO} ₄]	1.100, 2.111	Sn ^{IV} C ₂ (μ ₃ -O)(O _{ox}) ₂ , Sn ^{IV} C ₂ (μ ₃ -O) ₂ (N _{py})(N _{ox}); tbp, oct	[49]
[Zn ₄ (OH) ₂ Cl ₂ {(py)C(Me)NO} ₄]	2.111	Zn ^{II} (μ ₃ -OH)(O _{ox}) ₂ Cl, Zn ^{II} (μ ₃ -OH) ₂ N ₄ ; tetr, oct	this work

^a Solvate and other lattice molecules have been omitted; N_{ox} = oxime or oximate nitrogen; N_{py} = 2-pyridyl nitrogen; O_{nitr} = nitrate oxygen; O_{ox} = oximate oxygen; sp = square planar; spy = square pyramidal; tbp = trigonal bipyramidal; tetr = tetrahedral.

(py)C(Me)NO[−], because these ligands lack the second 2-pyridyl ring. It is worth mentioning that another zinc(II) metallacrown complex containing a 2-pyridyloximate ligand has been structurally characterized: this is [Zn₈(shi)₄{(py)₂CNO}₄(MeOH)₂], where shi^{3−} is the trianion of salicylhydroxamic acid [25]. The molecule contains a 12-MC-4 core constructed by four metal ions and four shi^{3−} ligands; the MC core accommodates a dinuclear Zn₂{(py)₂CNO}₄ component, while two of the ring metals create dinuclear units with the remaining two Zn^{II} ions through oxygen bridges. Since the MC ring is not constructed by the (py)₂CNO[−] ligands, this octanuclear cluster has not been included in Table 4.

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

(Fig. 4) is the exclusive one for the metal complexes containing the neutral ligands. Of particular note are the simultaneous presence of 1.011 (py)C(Me)NOH and (py)C(Me)NO[−] ligands in nickel(II) [43, 44] and rhodium(III) complexes [45]. The nature of R affects the structural motif of the organometallic complexes [R₈Sn₄O₂{(py)C(Me)NO}₄] [48, 49]. It should also be mentioned that the coordination modes 1.100 and 2.101, observed in organometallic compounds of antimony(V) [47] and tin (IV) [48, 49], are unique for the (py)C(R)NO[−] ligands (R = H, Me) [36].

Infrared characterization

A characteristic feature in the IR spectrum of **1** is the appearance of a strong broad band at 3200 cm^{−1} assignable [33] to ν(OH) of the neutral (py)C(Me)NOH ligand. The presence of hydroxo ligands in **2** is manifested by a medium broad band at 3414 cm^{−1} [32]. The broadness and relatively low frequency of these two bands are both indicative of strong hydrogen bonding.

Several bands appear in the 1620–1350 cm^{−1} range in the spectra **1** and **2**. Contributions from the

$\nu(\text{C}=\text{N})_{\text{oxime/oximate}}$ and $\delta(\text{CH}_3)$ modes would be expected in this region, but overlap with the stretching vibrations of the aromatic ring renders assignments and the discussion of the coordination shifts difficult. The medium bands at 1566 and 1116 cm^{-1} in the spectrum of the free ligand (py)C(Me)NOH are assigned to $\nu(\text{C}=\text{N})_{\text{oxime}}$ and $\nu(\text{N}-\text{O})_{\text{oxime}}$, respectively [50]. The 1116 cm^{-1} band is shifted to a lower wavenumber (1102 cm^{-1}) in **1** which contains the neutral form of the ligand. This shift is attributed to the coordination of the oxime nitrogen atom, in accord with the slightly longer N-O bonds in **1** (average length 1.390 Å) compared to this bond (1.406 Å) in the free ligand [48]. Somewhat to our surprise the 1566 cm^{-1} band is shifted to a higher wavenumber (1596 cm^{-1} , overlapping with an aromatic stretch) in **1**. This shift may be indicative of the oxime nitrogen coordination [51]. Extensive studies on Schiff-base complexes (which also contain a C=N bond) have shown [52] 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 C=N bond increases; this change in hybridization produces a greater C=N stretching force constant relative to the free neutral ligand. In accord with this concept the C=N bond lengths in **1** (average 1.277 Å) are not larger relative to the length of this bond in free [48] (py)C(Me)NOH (1.278 Å). We assign the 1544 and 1148 cm^{-1} bands of **2** to $\nu(\text{C}=\text{N})_{\text{oximate}}$ and $\nu(\text{N}-\text{O})_{\text{oximate}}$, respectively [50]. The frequency of the C=N stretching vibration has decreased from 1596 cm^{-1} in **1** to 1544 cm^{-1} in **2**, whereas the NO stretching vibration has increased from 1102 cm^{-1} in **1** to 1148 cm^{-1} in **2**. These inverse shifts are in accord with the concept [50] that upon deprotonation of the oxime group there is a higher contribution of N=O and a lower contribution of C=N to the electronic structure; consequently the $\nu(\text{CN})$ vibration shifts to a lower frequency and $\nu(\text{NO})$ to a higher frequency in **2**, both shifts relative to **1**. Indeed, the N-O bonds in **2** (average length 1.353 Å) are shorter than those in **1** (average length 1.390 Å).

The in-plane deformation band of the 2-pyridyl ring of free (py)C(Me)NOH at 632 cm^{-1} shifts upwards in **1** (638 cm^{-1}) and **2** (640 cm^{-1}), confirming the involvement of the ring N-atom in coordination [53].

Concluding Comments and Perspectives

The second use (see Table 4) of methyl 2-pyridyl ketone oxime in Zn chemistry has provided access to

two new zinc (II) chloro complexes, one mononuclear (**1**), and the other tetranuclear (**2**). In the former case, the ligand is neutral and chelates through its nitrogen atoms; in the latter case, the ligand is anionic, chelating and bridging a Zn^{II}_2 pair (Fig. 4). Complex **2** is a valuable addition to the small, but growing, family of inverse metallacrown complexes. The isolation and characterization of **2** also extends the body of results that emphasize the ability of the anionic ligand (py)C(Me)NO[−] (and, in general, of the anionic 2-pyridyl oximes) to form interesting structural types in coordination chemistry.

Work is in progress to clarify if the isothiocyanate, selenocyanate, cyanate, azide and dicyanamide derivatives of **2** have an inverse 12-MC-4 structure. The terminal chloro ligands of **2** could have future utility as sites for facile incorporation of bis(monodentate) bridging organic ligands as a means to get access to higher-nuclearity Zn^{II} clusters; experiments using dicarboxylate ligands are planned. Analogues of compound **2**, $[\text{Zn}_4(\text{OH})_2\text{Cl}_2\{(\text{py})\text{CHNO}\}_4]$ and $[\text{Zn}_4(\text{OH})_2\text{Cl}_2\{(\text{py})_2\text{CNO}\}_4]$ (see Table 4) with the remaining – commercially available – simple 2-pyridyl-aldoxime (Fig. 1), *i. e.* phenyl 2-pyridyl ketone oxime, 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 oxime ligand. We are currently studying this matter.

Experimental Section

All manipulations were performed under aerobic conditions using materials and solvents (Merck, Aldrich) as received. The free ligand (py)C(Me)NOH was synthesized by the reaction of equimolar quantities of 1-pyridin-2-yl-ethanone (2-acetylpyridine), (py)C(Me)O, $\text{H}_2\text{NOH} \cdot \text{HCl}$ and NaOEt in EtOH, as described by Saarinen and co-workers [54]. The crude material was recrystallized twice from benzene, m.p. 119 °C (literature [54] 120 °C). Elemental analyses (C, H, N) were conducted at the University of Ioannina, Greece, Microanalytical Service using an EA 1108 Carlo Erba analyser. IR spectra (4000–500 cm^{-1}) were recorded on a Perkin-Elmer 16PC FT spectrometer with samples prepared as KBr pellets.

$[\text{ZnCl}_2\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_2]$ (**1**)

A colourless solution of ZnCl_2 (0.14 g, 1.0 mmol) in EtOH (10 ml) was added to a slurry of (py)C(Me)NOH (0.14 g, 1.0 mmol) in MeCN (10 ml). The resulting colourless solution was stirred for about 4 h and was then allowed to slowly concentrate by solvent evaporation at room tem-

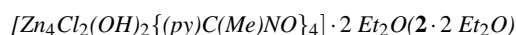
Table 6. Summary of crystal data, data collection and structure refinement for the X-ray diffraction study of complexes **1** and **2** · 2 Et₂O.

Complex	1	2 · 2 Et ₂ O
Chemical formula	C ₁₄ H ₁₆ Cl ₂ N ₄ O ₂ Zn	C ₃₆ H ₅₀ Cl ₂ N ₈ O ₈ Zn ₄
Formula weight	408.58	1055.22
Colour, habit	colourless prisms	colourless 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]	8.775(4)	12.230(10)
<i>b</i> [Å]	10.771(5)	14.640(10)
<i>c</i> [Å]	18.304(9)	12.730(10)
β [deg]	92.44(2)	90.96(3)
<i>V</i> [Å ³]	1728.4(14)	2279(3)
<i>Z</i>	4	4
<i>D</i> _{calc} [g cm ⁻³]	1.570	1.538
μ [mm ⁻¹]	1.743	2.252
<i>F</i> (000)	832	1080
Radiation [Å]	Mo-K α	Mo-K α
	(λ = 0.71073)	(λ = 0.71073)
Temperature [K]	293(2)	293(2)
Scan mode/speed	θ -2 θ /5	θ -2 θ /5
[deg min ⁻¹]		
θ Range [deg]	2.19–25.00	2.17–24.94
Ranges <i>h</i>	–10 → 0	–13 → 14
<i>k</i>	–12 → 0	0 → 16
<i>l</i>	–21 → 21	0 → 13
Measured reflections	3260	3246
Unique reflections	3049	3099
	(<i>R</i> _{int} = 0.0181)	(<i>R</i> _{int} = 0.0503)
Reflections used		
[<i>I</i> > 2 σ (<i>I</i>)]	2727	2608
Parameters refined	272	280
<i>w</i> ^a	<i>a</i> = 0.0146; <i>b</i> = 0.5923	<i>a</i> = 0.1085; <i>b</i> = 4.2129
GoF (on <i>F</i> ²)	1.055	1.038
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0256	0.0559
<i>wR</i> 2 ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.0665	0.1537
$\Delta\rho$ _{max} /($\Delta\rho$) _{min}	0.477/–0.327	0.981/–0.695
[e Å ⁻³]		

^a $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$;

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

perature for a period of 1–2 d. Well-formed X-ray quality colourless prismatic crystals appeared which were collected by filtration, washed with Et₂O (3 ml) and dried in air. Typical yields were in the 50–60% range. IR (KBr pellet): ν = 3200, 3120, 3068, 1596, 1480, 1448, 1380, 1324, 1258, 1164, 1140, 1102, 1042, 964, 786, 748, 682, 638, 552, 451 cm⁻¹ – C₁₄H₁₆N₄O₂Cl₂Zn (408.58): calcd. C 41.15, H 3.96, N 13.72; found C 41.33, H 3.88, N 14.60.



A colourless solution of ZnCl₂ (0.14 g, 1.0 mmol) in EtOH (10 ml) was added to a slurry of (py)C(Me)NOH (0.14 g, 1.0 mmol) and LiOH·H₂O (0.04 g, 1.0 mmol) in MeCN (10 ml). The reaction mixture was stirred for about 3 h, and then filtered and layered with Et₂O. Slow mixing gave well-formed, X-ray quality colourless prismatic crystals, which were collected by filtration, washed with cold H₂O (2 × 1 ml), EtOH (2 ml) and Et₂O (3 ml) and dried *in vacuo* over silica gel. Typical yields were in 60–70% range. IR (KBr pellet): ν = 3414, 3070, 3025, 1598, 1544, 1476, 1440, 1376, 1256, 1148, 1072, 978, 784, 702, 640, 558, 506 cm⁻¹. The dried solid analysed satisfactorily as Et₂O-free. C₂₈H₃₀N₈O₆Cl₂Zn₄ (906.96): calcd. C 37.08, H 3.34, N 12.36; found C 36.90, H 3.40, N 12.20.

Crystal structure determinations

Colourless prismatic crystals of **1** (0.25 × 0.25 × 0.70 mm) and **2** · 2 Et₂O (0.20 × 0.30 × 0.35 mm) were mounted in air; the crystals of **2** · 2 Et₂O had been previously covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Crystal data and full details of the data collection and data processing are listed in Table 6. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11 < 2 θ < 23°. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86 [55] and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [56]. All H atoms for structure **1** and some of the H atoms for structure **2** were located by difference maps and refined isotropically. For both structures all non-H atoms were refined using anisotropic displacement parameters. Two X-ray crystallographic files for **1** and **2** · 2 Et₂O in CIF format have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, under the numbers 283299 (**1**) and 283300 (**2** · 2 Et₂O). Copies may be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

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