Di-2-pyridyl Ketone Oxime in Zinc Chemistry: Inverse 12-Metallacrown-4 Complexes and Cationic Pentanuclear Clusters

Maria Alexiou,[a] Eugenia Katsoulakou,[b] Catherine Dendrinou-Samara,[a]
Catherine P. Raptopoulou,[c] Vassilis Psycharis,[c] Evy Manessi-Zoupa,[b]
Spyros P. Perlepes,*[b] and Dimitris P. Kessissoglou*[a]

Keywords: Cluster compounds / Inverse metallacrowns / Oximato complexes / X-ray crystallography / Zinc

The use of di-2-pyridyl ketone oxime (Hpko)/X^- "blends" (X^- = $PhCO_2^-$, N_3^-, NCO^-, $acac^-$, NCS^-) in zinc chemistry yields neutral tetranuclear and cationic pentanuclear clusters. Various synthetic procedures have led to the synthesis of compounds $[Zn_4(OH)_2(O_2CPh)_2(pko)_4]\cdot 3MeCN$ (**1**·3MeCN), $[Zn_4(OH)_2(N_3)_2(pko)_4]\cdot 4DMF$ (**2**·4DMF), $[Zn_4(OH)_2(NCO)_2(pko)_4]\cdot 3DMF\cdot H_2O$ (**3**·3DMF·H_2O), $[Zn_4(OH)_2(acac)_2(pko)_4]\cdot 4CH_2Cl_2$ (**4**·4CH_2Cl_2), $[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]\cdot 2.5H_2O\cdot 1.5MeOH$ (**5**·2.5H_2O·1.5MeOH) and $[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]\cdot 2.5H_2O\cdot MeOH$ (**6**·2.5H_2O·MeOH). The structures of the six complexes have been determined by single-crystal X-ray crystallography. The tetranuclear molecules of **1**–**4** lie on a crystallographic inversion centre and have an inverse 12-metallacrown-4 topology. Two triply bridging hydroxides are accommodated in the centre of the metallacrown ring. The pko^- ligands form a propeller configuration that imposes absolute stereoisomerism with Λ and Δ chirality. Two metal ions are in distorted O_2N_4 octahedral environments, whereas the rest are in severely distorted tetrahedral or trigonal bipyramidal environments. The five Zn ions of the cations of **5** and **6** are held together by six pko^- ligands which adopt three different coordination modes; the chloro (**5**) and isothiocyanato (**6**) ligands are terminal. The five Zn ions define two nearly equilateral triangles sharing a common apex, and the novel Zn_5 topology can be described as two "collapsed" 9-metallacrown-3 structures sharing a common Zn apex. Besides the pentanuclear cations, the structures of **5** and **6** contain slightly distorted tetrahedral $[ZnCl(NCS)_3]^{2-}$ and $[Zn(NCS)_4]^{2-}$ ions, respectively, with the isothiocyanato ligands binding the metal ion in a virtually linear fashion.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Metallamacrocycles have gained increasing attention over the past decade due to their potentially unique properties. These molecules have already been used in applications as diverse as catalysis,[1] sensors[2] or as chiral building blocks for two and three-dimensional solids.[3] Metallamacrocycles include complexes such as metallacrowns,[4] metallacrowns containing carbon in the macrocycle,[5] azametallacrowns,[6] anticrowns,[7] metallacrown ethers,[8] metallahelicates,[9] metallacalixarenes,[10] metallacryptates,[11] molecular squares and boxes[1,2,12]and polynuclear alkoxo- or oxometal complexes.[13]

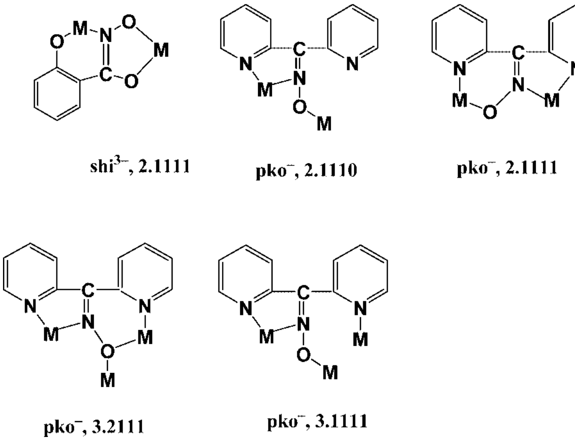
Metallacrowns (MCs),[4] the inorganic structural and functional analogues of crown ethers,[14] are usually formed with transition metal ions and a nitrogen replacing the methylene carbon atoms. MCs exhibit selective recognition of cations and anions, and can display intramolecular magnetic-exchange interactions. The isolation of MCs 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. The first MCs were prepared using the triply deprotonated form (shi^{3-}) of salicylhydroxamic acid as ligand.[4,15] This dinucleating agent contains four heteroatoms that are potential metal-binding sites: one metal atom can bind in a five-membered chelate ring formed through the hydroximate group while a second metal atom can bind in a six-membered chelate ring through the iminophenolate group, i.e., shi^{3-} can act as a 2.1111 ligand using Harris notation.[16] This approach yields clusters with M–N–O–M networks linking the ring metal atoms and forms the basis of MCs (Figure 1). The synthesis of MCs is not necessarily restricted to the use of organic ligands with a hydroximate moiety, however. The same M–N–O–M connectivity can be achieved using oximate ligands that can form six- and/or five-membered chelate rings.[4] One example of such a ligand is di-2-pyridyl ketone oxime (Hpko),[17] whose anion (pko^-) can adopt a variety of coordination modes (Figure 1); pko^- is the ligand used in the present study. Even

---

[a] Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki,
54124 Thessaloniki, Greece
E-mail: kessisog@chem.auth.gr
[b] Department of Chemistry, University of Patras,
26504 Patras, Greece
E-mail: perlepes@patreas.upatras.gr
[c] Institute of Materials Science, NCSR "Demokritos",
15310 Aghia Paraskevi Attikis, Greece

DOI: 10.1002/ejic.200400933

more interesting are MCs composed of a combination of oximate and hydroximate ligands, e.g., pko$^-$ and shi^{3-}.[4,18]



shi^{3-}, 2.1111 pko$^-$, 2.1110 pko$^-$, 2.1111

pko$^-$, 3.2111 pko$^-$, 3.1111

Figure 1. Some of the crystallographically established coordination modes of the ligands shi^{3-} and pko$^-$ discussed in the text, and the Harris notation that describes these modes.

Metallacrown nomenclature is discussed in several key references.[4,18,19] There are now examples of [9-$\mathrm{MC}_{\mathrm{M(ox)N(ligand)}}$-3],[20] [12-$\mathrm{MC}_{\mathrm{M(ox)N(ligand)}}$-4],[15,18,19,21] [15-$\mathrm{MC}_{\mathrm{M(ox)N(ligand)}}$-5][19,22] and [24-$\mathrm{MC}_{\mathrm{M(ox)N(ligand)}}$-8][17] structural types, as well as fused, dinuclear and mixed-metal MCs.[4,18,19,23] There are nine metals in four oxidation states (II–V) that have been incorporated into the MC ring, while more than 20 metal ions, i.e., lanthanide, actinide, alkali, alkaline earth and transition metal ions have been captured in the central cavity of MCs.

For 12-MC-4 complexes, two structural motifs have been reported: classical or regular[15,18,19,21] and inverse,[24] 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 centre of the cavity and capable of binding cations.[4] In the inverse motif, which has been realized only for Zn[24] and Co,[25] the ring metal ions are oriented towards the centre of the cavity which is now capable of encapsulating anions, whereas the connectivity is transposed to N–O–M–O–N–M.

Our groups have been exploring the chemistry of MCs[17,19,21a,21e,22a,22f,23b,24b,25] and the coordination chemistry of 2-pyridyl oximes,[26,27] the latter not necessarily in relation to the former. There is currently a renewed interest in the coordination chemistry of oximes.[28] Research efforts are driven by a number of considerations, including the solution of pure chemical problems,[29] the development of new oxygen activation catalysts,[30] the application of metal/oxime systems as simple and efficient catalysts for the hydrolysis of organonitriles,[31] the mechanistic study of corrosion inhibition by Acorga P5000 (a modern corrosion inhibitor) on Fe surfaces,[32] and the employment of oximate ligands in the synthesis of homometallic or heterometallic clusters[28a,33,34] and chains[35] with interesting magnetic properties, including single-molecule magnetism[34e] and single-chain magnetism[35] behaviour. For example, the pure chemical interest arises from the ability of the oximate(1–) group (–C=N–O$^-$) to stabilize higher metal oxidation states,[36] such as Ni$^{\mathrm{III}}$ or Ni$^{\mathrm{IV}}$, and the fact that the activation of oximes by transition metal centres towards further reactions seems to be an excellent area of modern synthetic chemistry.[28] In contrast to the great number of studies concerning metal complexes of simple oximes and salicylaldoxime,[28,34d,32] little is known about complexes of pyridyl oximes, although this class of compounds could offer unique features in terms of structural characteristics and physical properties.

Di-2-pyridyl ketone oxime (Hpko) occupies a special position amongst the 2-pyridyl oximes. One area to which the ligand pko$^-$ is relevant is the chemistry of MCs (see above). Another attractive aspect of pko$^-$ is its great coordinative flexibility and versatility, characteristics that have led to polynuclear 3d-metal complexes with impressive structures and interesting magnetic properties.[26,27a,27e,37] A last interesting feature is the activation of Hpko by 3d-metal centres, which appears to be a fruitful area of synthetic inorganic chemistry. Examples of this activation are the Mn-assisted transformation of Hpko into the coordinated dianion of the *gem*-diol form of di-2-pyridyl ketone through NO_3^- generation,[27a] and the in-situ transformation of Hpko into the coordinated ligands di-2-pyridylimine, (amino)di-2-pyridylmethyl ethyl ether and (amino)di-2-pyridylmethyl methyl ether upon its reaction with [$\mathrm{V^{III}Cl_3(THF)_3}$] in various solvents.[38]

Zinc(II)/Hpko chemistry has attracted some prior interest. Pecoraro and co-workers have prepared the tetranuclear species [$\mathrm{Zn_4(OH)_2(O_2CMe)_2(pko)_4}$] or {$\mathrm{(OH)_2}$[inv12-$\mathrm{MC}_{\mathrm{Zn^{II}N(pko)}}$-4]($\mathrm{O_2CMe}$)$_2$}[24a] (using the metallacrown nomenclature), which is the archetype of the inverse 12-MC-4 complexes. Some of us have also prepared and studied[24b] [$\mathrm{ZnCl_2(Hpko)}$], [$\mathrm{Zn_4(OH)_2Cl_2(pko)_4}$] or{$\mathrm{(OH)_2}$[inv12-$\mathrm{MC}_{\mathrm{Zn^{II}N(pko)}}$-4]$\mathrm{Cl_2}$} and [$\mathrm{Zn_8(shi)_4(pko)_4(MeOH)_2}$]; the second of these complexes is also an inverse 12-MC-4 species, while a part of the octanuclear cluster can be described as having a formally anionic [12-$\mathrm{MC}_{\mathrm{Zn^{II}N(shi)}}$-4]$^{4-}$ core with the 12-membered ring acting as host agent for a dinuclear $\mathrm{Zn_2(pko)_4}$ unit and with two of the MC ring Zn$^{\mathrm{II}}$ ions creating dinuclear moieties with the remaining metal ions. Using these prior observations as a starting point and seeking to extend the family of the inverse 12-$\mathrm{MC}_{\mathrm{Zn^{II}N(pko)}}$-4 complexes, to incorporate pseudohalides (N_3^-, NCO$^-$, SCN$^-$), carboxylates other than acetates or anionic chelates into the Zn$^{\mathrm{II}}$/pko$^-$ chemistry, and to examine the possibility of creating novel cluster topologies within this chemistry, we report here the successful development of synthetic routes to cationic pentanuclear Zn$^{\mathrm{II}}$/pko$^-$ clusters and to new examples of inverse 12-$\mathrm{MC}_{\mathrm{Zn^{II}N(pko)}}$-4 compounds featuring N_3^-, NCO$^-$, SCN$^-$, $\mathrm{PhCO_2^-}$ or acac$^-$ coligands [acac = acetylacetonate(–1) ion].

Results and Discussion

Synthesis

As stated above, we were interested in extending the very small family of inverse 12-MC$_{Zn^{II}N(pko)}$-4 complexes. In an earlier report, Pecoraro's group reported the preparation of the inverse metallacrown $[Zn_4(OH)_2(O_2CMe)_2(pko)_4]$.[24a] Thus, we decided to seek the benzoate version of this complex. Our main goal was to determine whether the benzoate cluster would have a similar molecular structure. The preparation of compound **1** can be achieved by the 1:1 reaction of $Zn(O_2CPh)_2{\cdot}2H_2O$ with pko$^-$ in MeCN at room temperature [Equation (1)]. Note that both Et_3N and the released $PhCO_2^-$ groups can act as proton acceptors to facilitate formation of OH^- and pko$^-$ ligands.

$$4\,Zn(O_2CPh)_2{\cdot}2H_2O + 4\,Hpko + 4\,Et_3N \xrightarrow{MeCN} \underset{\mathbf{1}}{[Zn_4(OH)_2(O_2CPh)_2(pko)_4]} + 2\,PhCO_2H + 4\,Et_3NHO_2CPh + 6\,H_2O \quad (1)$$

Similar results were obtained in the absence of the external Et_3N base; however, the yield (about 20%) was lower. The formation of **1** in the absence of Et_3N (not reported in the Experimental Section) is summarised by Equation (2).

$$4\,Zn(O_2CPh)_2{\cdot}2H_2O + 4\,Hpko \xrightarrow{MeCN} \underset{\mathbf{1}}{[Zn_4(OH)_2(O_2CPh)_2(pko)_4]} + 6\,PhCO_2H + 6\,H_2O \quad (2)$$

Two years ago we reported[24b] the preparation of the inverse 12-MC-4 $[Zn_4(OH)_2Cl_2(pko)_4]$ from the reaction of $ZnCl_2$ with pko$^-$ or by addition of NaOH to a MeOH/DMF solution of the mononuclear complex $[ZnCl_2(Hpko)]$. We wondered whether pseudohalide analogues of the chloro cluster could be prepared. For example, we could envisage that complexes $[Zn_4(OH)_2X_2(pko)_4]$ ($X = N_3^-$, SCN^-, OCN^-, ...), with two terminal X^- ligands instead of two terminal chloro ligands, should be stable. Reactions between convenient Zn^{II} sources and a combination of N_3^- or OCN^- and pko$^-$ (ca. 2:1:2) in DMF or DMF/MeOH led to subsequent isolation of pure crystalline complexes **2** and **3** in good yields (ca. 70%) [Equations (3) and (4)]. Single-crystal X-ray crystallography revealed the expected structural similarity between **2** and **3** and the chloro cluster.

$$4\,Zn(NO_3)_2{\cdot}4H_2O + 2\,NaN_3 + 4\,Hpko + 4\,NaOH \xrightarrow{DMF} \underset{\mathbf{2}}{[Zn_4(OH)_2(N_3)_2(pko)_4]} + 6\,NaNO_3 + 2\,HNO_3 + 18\,H_2O \quad (3)$$

$$4\,ZnCl_2 + 2\,NaOCN + 4\,Hpko + 4\,NaOH \xrightarrow{DMF/MeOH} \underset{\mathbf{3}}{[Zn_4(OH)_2(NCO)_2(pko)_4]} + 6\,NaCl + 2\,HCl + 2\,H_2O \quad (4)$$

Two features of the Equations (3) and (4) deserve comments. First, the reaction "solutions" should be filtered before crystallisation to remove a small amount of $NaNO_3$ or NaCl which remains insoluble in DMF. Second, the employment of DMF is beneficial to the syntheses as DMF solvate molecules stabilize the crystal lattices of **2** and **3** and also possibly aid in the "neutralisation" of the produced *dilute* HCl or HNO_3 and, thus, the latter do not decompose the hydroxo clusters.

The next questions we addressed were whether the monodentate ligands $PhCO_2^-$, N_3^-, OCN^- and Cl^- in **1**, **2**, **3** and $[Zn_4(OH)_2Cl_2(pko)_4]$,[24b] respectively, or the *nearly* monodentate $MeCO_2^-$ ligand (in fact the acetato ligand is anisobidentate) in $[Zn_4(OH)_2(O_2CMe)_2(pko)_4]$,[24a] could be replaced by anionic chelates and whether this replacement would preserve the inverse 12-MC-4 structural type. The anionic chelating ligand chosen was the acetylacetonate(–1) ion (acac$^-$). The procedure that leads to pure **4** involves the reaction of $Zn(acac)_2{\cdot}H_2O$ with an almost equimolar amount of Hpko in CH_2Cl_2 under reflux [Equation (5)]. The source of the hydroxo ligands is moisture from the starting materials, and the solvents used for the preparation (CH_2Cl_2) and/or crystallisation (Et_2O) of the complex. Single-crystal X-ray crystallography revealed the existence of an inverse 12-MC-4 motif in **4**. The isolation of the hydroxo cluster **4** from non-polar solvents is strong evidence of the great thermodynamic stability of the $\{Zn_4(\mu_3\text{-}OH)_2(pko)_4\}^{2+}$ unit.

$$4\,Zn(acac)_2{\cdot}H_2O + 4\,Hpko \xrightarrow[T]{CH_2Cl_2} \underset{\mathbf{4}}{[Zn_4(OH)_2(acac)_2(pko)_4]} + 6\,Hacac + 2\,H_2O \quad (5)$$

We initially came across complexes **5** and **6** when we tried to prepare the isothiocyanato analogue of $[Zn_4(OH)_2Cl_2(pko)_4]$, **2** and **3**. These at first glance trivial efforts led to dramatic nuclearity and structural changes. The initial reaction explored was that between $ZnCl_2$, half an equivalent of SCN^- and one equivalent of pko$^-$ (prepared in situ from Hpko and NaOH) in MeOH. The colourless solution obtained gradually turned to pale yellow upon stirring. Concentration of the resulting solution at room temperature gave a mixture of colourless prisms and pale-yellow needles. Their not-too-dissimilar solubility prevented chemical separation; however, the differences in colour and crystal shape allowed manual separation of the two materials. The colourless and pale-yellow crystals were crystallographically identified as complexes $[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]{\cdot}2.5H_2O{\cdot}1.5MeOH$ (**5**$\cdot 2.5H_2O{\cdot}1.5MeOH$) and $[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]{\cdot}2.5H_2O{\cdot}MeOH$ (**6**$\cdot 2.5H_2O{\cdot}MeOH$), respectively. Stoichiometric reactions of the formation of **5** and **6** are represented by Equations (6) and (7), respectively.

With the identities of **5** and **6** established, convenient syntheses of pure materials were sought under alternative reaction conditions. Complex **6** has a Zn^{II}/SCN^- ratio of 1:1, whereas the initial reaction solution had a Zn^{II}/SCN^- ratio

$$6\,ZnCl_2 + 3\,NaSCN + 6\,Hpko + 6\,NaOH \xrightarrow{MeOH} \underset{\mathbf{5}}{[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]} + 9\,NaCl + 6\,H_2O \tag{6}$$

$$6\,ZnCl_2 + 6\,NaSCN + 6\,Hpko + 6\,NaOH + MeOH \xrightarrow{MeOH} \underset{\mathbf{6}}{[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]} + 12\,NaCl + 6\,H_2O \tag{7}$$

of 2:1; thus, attempts to obtain pure **6** were made by decreasing this ratio. Somewhat to our disappointment, the use of $ZnCl_2$/NaSCN ratios of 1:1 or even of 1:2 again gave mixtures of **5** and **6**. It is likely that the reaction solution contains a complicated mixture of several species in equilibrium, with factors such as relative solubility, lattice energy, crystallisation kinetics amongst others determining the identity of the isolated products. Since complex **6** is chloride-free, the next logical step to prepare the pure compound was to exclude Cl^- ions from the reaction mixture. The preparation of pure **6** was achieved by the reaction of a slight excess of $Zn(O_2CMe)_2{\cdot}2H_2O$ with one equivalent of NaSCN and one equivalent of Hpko in MeOH [Equation (8)].

$$6\,Zn(O_2CMe)_2{\cdot}2H_2O + 6\,NaSCN + 6\,Hpko + MeOH \xrightarrow{MeOH} \underset{\mathbf{6}}{[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]} + 6\,NaO_2CMe + 6\,MeCO_2H + 12\,H_2O \tag{8}$$

In seeking to prepare the pure complex **5**, it was logical to carry out reactions employing high $ZnCl_2$/NaSCN ratios. The 3:1:3 and 4:1:4 $ZnCl_2$/NaSCN/pko^- reaction mixtures in MeOH led to precipitation of *almost* pure colourless **5** in good yields (typically higher than 50%). However, careful examination of the crystalline powders from these reactions revealed trace amounts of pale-yellow microcrystals and/or specks which were shown to be complex **6** by IR spectroscopy. Thus, the manual separation of colourless crystals from their above-described mixtures with **6** remains the only source of complex **5** to date for further measurements.

Since complexes **5** and **6** contain different Zn^{II}/SCN^- ratios, it seemed reasonable to suspect that they could be interconverted by treatment of the performed materials with appropriate reagents. The conversion of **5** to **6** can be accomplished quite easily by treatment of the former with an excess of NaSCN in MeOH at 45 °C [Equation (9)]. Addition of a small amount of external H_2O to the reaction mixture is necessary to achieve a clean conversion of **5** to **6**, presumably by keeping the produced NaCl soluble. All efforts to prepare **5** by the reaction of **6** with an excess of NaCl in MeOH or MeOH/H_2O were in vain.

$$\underset{\mathbf{5}}{[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]} + 3\,NaSCN + MeOH \xrightarrow[45\,^{\circ}C,\ exc.\ NaSCN]{MeOH/H_2O\ (10:1\ v/v)} \underset{\mathbf{6}}{[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]} + 3\,NaCl \tag{9}$$

The isolation of **5** and **6** was surprising and, needless to say, unexpected. We suspected that the formation of the pentanuclear clusters might be related to their cationic character. Thus, we tried to prepare such clusters with N_3^- and OCN^- ligands under conditions that favour formation of anionic compounds, i.e., employing bulky non-coordinating counteranions. Synthetic studies of hundreds of ZnX_2/OCN^- or N_3^-/pko^-/Y^- reaction mixtures (X = Cl, NO_3, $MeCO_2$; Y = PF_6, ClO_4, BPh_4) repeatedly led to microcrystalline materials. Analytical data were consistent with the formulation $[Zn_5(OCN)_2(pko)_6]Y_2$ or $[Zn_5(N_3)_2(pko)_6]Y_2$ and IR data indicated the presence of Y^- counterions, but, unfortunately, numerous attempts to obtain crystals suitable for crystallographic studies all were in vain. We were luckier, but at the same time unlucky again, when we employed $acac^-$ (instead of N_3^- or OCN^-) in the above-mentioned reaction mixtures. The reaction, summarised in Equation (10), gave pale-yellow prisms, which were proven to be single crystals.[39] Unfortunately, the crystals were of bad quality and poor diffractors of X-rays and, therefore, we refrain from presenting a full structural analysis here. Nevertheless, single-crystal crystallographic studies clearly revealed the presence of the $[Zn_5(acac)_2(pko)_6]^{2+}$ ion in the product, further emphasising our belief that the pentanuclear clusters are isolable only as cations.

$$5\,Zn(acac)_2{\cdot}H_2O + 6\,Hpko + 3\,NH_4PF_6 \xrightarrow{MeOH} (NH_4)[Zn_5(acac)_2(pko)_6](PF_6)_3 + 6acacH + 2\,NH_4acac + 5\,H_2O \tag{10}$$

Description of Structures

$[Zn_4(OH)_2(O_2CPh)_2(pko)_4]{\cdot}3MeCN$ ($\mathbf{1}{\cdot}3MeCN$), $[Zn_4(OH)_2(N_3)_2(pko)_4]{\cdot}4DMF$ ($\mathbf{2}{\cdot}4DMF$), $[Zn_4(OH)_2(NCO)_2(pko)_4]{\cdot}3DMF{\cdot}H_2O$ ($\mathbf{3}{\cdot}3DMF{\cdot}H_2O$) and $[Zn_4(OH)_2(acac)_2(pko)_4]{\cdot}4CH_2Cl_2$ ($\mathbf{4}{\cdot}4CH_2Cl_2$)

Partially labelled plots of the tetranuclear molecules present in compounds **1**·3MeCN, **2**·4DMF, **3**·3DMF·H_2O and **4**·4CH_2Cl_2, are shown in Figures 2, 3, 4, and 5, respectively. Selected interatomic distances and angles are listed in Tables 1, 2, 3, and 4, respectively. The molecular structures of the four complexes are similar in many aspects and, thus, only the structure of the representative complex **1**·3MeCN will be described in detail.

The tetranuclear molecule of **1**·3MeCN lies on a crystallographic inversion centre and has a planar, nearly rhombic arrangement of the metal centres. The two diagonals of the rhombus correspond to the interatomic distances Zn(1)···Zn(1′) and Zn(2)···Zn(2′) which are equal to 5.815(1) and 3.224(1) Å, respectively, the short diagonal being very similar to the sides of the rhombus. Due to the presence of the crystallographic inversion centre, the $\{Zn(2)Zn(2')O(21)O(21')\}^{2+}$ subcore is strictly planar. The metallacrown is characterised as inverse because the Zn ions, rather than the oximate oxygen atoms, are oriented towards the centre of the cavity, while the connectivity is

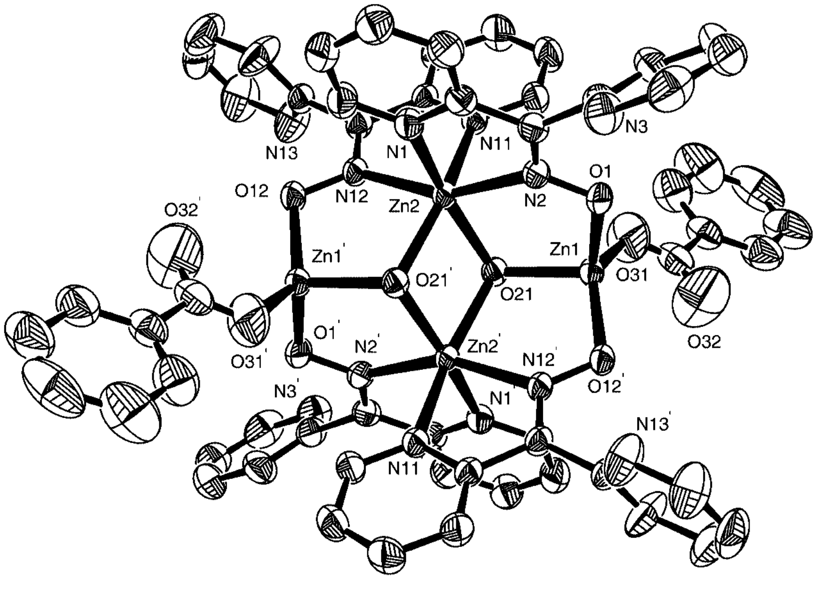


Figure 2. Partially labelled ORTEP plot of the tetranuclear molecule of complex **1**·3MeCN. Primed and unprimed atoms are related by the crystallographic inversion centre. O(21) and O(21′) are the hydroxo oxygen atoms. The connectivity of the inverse metallacrown ring has been highlighted.

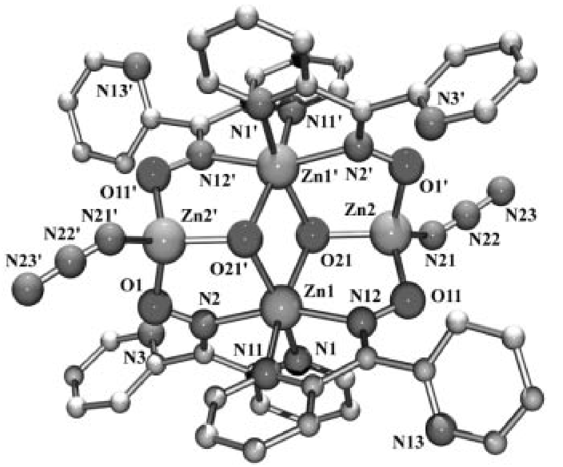


Figure 3. Partially labelled POV-RAY plot of the tetranuclear molecule of complex **2**·4DMF. Other details are as in the caption of Figure 2.

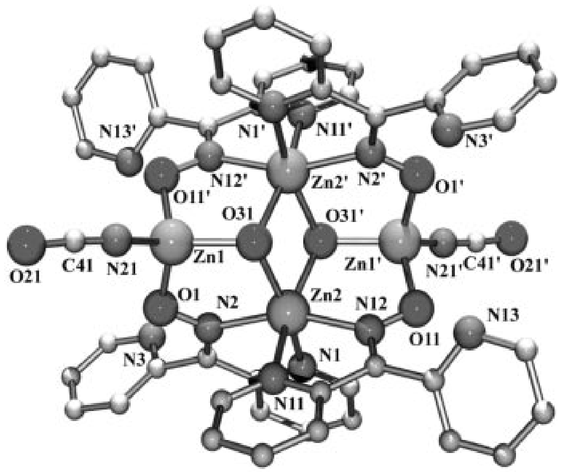


Figure 4. Partially labeled POV-RAY plot of the tetranuclear molecule of complex **3**·3DMF·H_2O. Primed and unprimed atoms are related by the crystallographic inversion centre. O(31) and O(31′) are the hydroxo oxygen atoms. The connectivity of the inverse metallacrown ring has been highlighted.

N–O–Zn–O–N–Zn. The Zn centres are bridged along each side of the rhombus by one μ_3-hydroxide [O(21),O(21′)] and one oximate(–1) group. The pko$^-$ ligands adopt an η^1:η^1:η^1:μ_2 (or 2.1110[16]) coordination mode. The coordination about the hydroxo oxygen atom, O(21), is markedly pyramidal [sum of Zn–O(21)–Zn angles: 319.7°].

The metal ions exhibit two coordination geometries. Zn(2) and Zn(2′) are in distorted O_2N_4 octahedral environments, whereas Zn(1) and Zn(1′) are in severely distorted O_4 tetrahedral environments. Each hydroxo oxygen atom bridges to two octahedral Zn ions and one tetrahedral Zn ion. The octahedral Zn ions are bound to two pko$^-$ moieties by pyridyl nitrogen atoms [N(1), N(11), N(1′), N(11′)] and the oxime nitrogen atoms [N(2), N(12), N(2′), N(12′)] in two five-membered chelating rings. The remaining two coordination sites of the octahedron are filled by the two μ_3-hydroxide ions accommodated in the centre 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′). Each tetrahedral Zn ion is bound to one of the bridging hydroxo ligands and to two oximate oxygen atoms, while the fourth site is occupied by an oxygen atom [O(31), O(31′)] from a coordinated benzoate ion. The longer Zn(2)–O bonds [2.085(3), 2.088(4) Å] compared to the Zn(1)–O ones [1.925(5)–1.991(3) Å] are a consequence of the higher coordination number of Zn(2). The angles around Zn(1) [and Zn(1′)] are in the wide 100.9(3)–133.3(2)° range. The benzoate oxygen atom [O(31)] forms a strong bond with Zn(1) [1.925(5) Å]. As is sometimes (but not always) observed for monodentate RCO_2^- groups, there

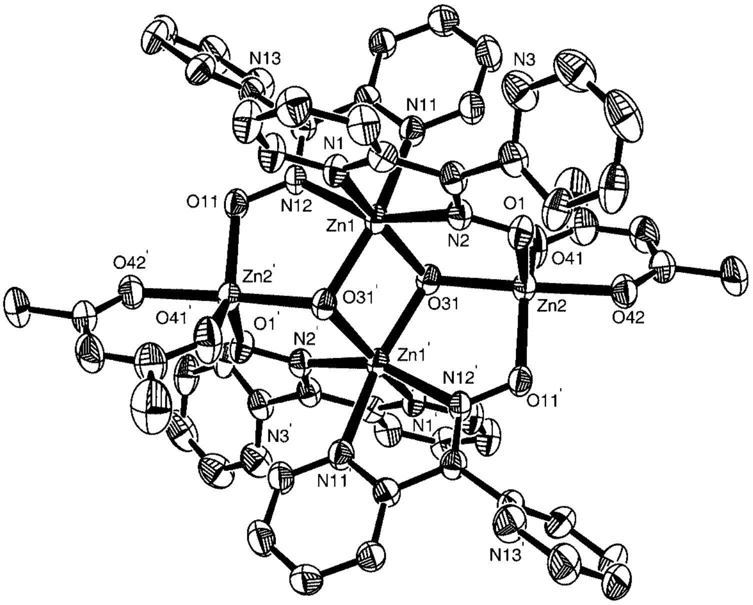


Figure 5. Partially labeled ORTEP plot of the tetranuclear molecule of complex **4**·$4CH_2Cl_2$. Other details are as in the caption of Figure 4.

Table 1. Selected interatomic distances [Å] and angles [°] for $[Zn_4(OH)_2(O_2CPh)_2(pko)_4]\cdot 3MeCN$ (**1**·3MeCN).[a]

Zn(1)···Zn(2)	3.334(1)	Zn(1)–O(31)	1.925(5)
Zn(1)···Zn(2′)	3.315(1)	Zn(2)–O(21)	2.088(4)
Zn(1)···Zn(1′)	5.815(1)	Zn(2)–O(21′)	2.085(3)
Zn(2)···Zn(2′)	3.224(1)	Zn(2)–N(1)	2.196(4)
Zn(1)–O(1)	1.974(3)	Zn(2)–N(11)	2.187(3)
Zn(1)–O(12′)	1.951(3)	Zn(2)–N(2)	2.156(3)
Zn(1)–O(21)	1.991(3)	Zn(2)–N(12)	2.158(3)
O(1)–Zn(1)–O(12′)	106.0(1)	N(2)–Zn(2)–N(12)	156.4(1)
O(12′)–Zn(1)–O(31)	133.3(2)	Zn(1)–O(21)–Zn(2)	108.7(2)
O(21)–Zn(1)–O(31)	100.9(3)	Zn(1)–O(21)–Zn(2′)	109.8(1)
O(21)–Zn(2)–N(1)	161.2(1)	Zn(2)–O(21)–Zn(2′)	101.2(2)
O(21′)–Zn(2)–N(11)	158.6(1)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x* + 1, –*y*, –*z* + 1.

Table 2. Selected interatomic distances [Å] and angles [°] for $[Zn_4(OH)_2(N_3)_2(pko)_4]\cdot 4DMF$ (**2**·4DMF).[a]

Zn(1)···Zn(2)	3.312(1)	Zn(2)–N(21)	1.925(5)
Zn(1)···Zn(2′)	3.301(1)	Zn(1)–O(21)	2.122(3)
Zn(1)···Zn(1′)	3.243(1)	Zn(1)–O(21′)	2.103(3)
Zn(2)···Zn(2′)	5.763(1)	Zn(1)–N(1)	2.171(4)
Zn(2)–O(1′)	1.964(3)	Zn(1)–N(11)	2.194(4)
Zn(2)–O(11)	1.966(3)	Zn(1)–N(2)	2.153(3)
Zn(2)–O(21)	1.953(3)	Zn(1)–N(12)	2.144(3)
O(1′)–Zn(2)–O(11)	102.0(1)	Zn(2)–O(21)–Zn(1)	108.7(2)
O(21)–Zn(2)–N(21)	119.5(2)	Zn(2)–O(21)–Zn(1′)	108.9(2)
O(21)–Zn(1)–N(11)	159.3(1)	Zn(1)–O(21)–Zn(1′)	100.3(1)
O(21′)–Zn(1)–N(1)	159.2(1)	Zn(2)–N(21)–N(22)	134.0(7)
N(2)–Zn(1)–N(1)	160.5(1)	N(21)–N(22)–N(23)	175.8(12)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x*, –*y*, –*z* + 1.

Table 3. Selected interatomic distances [Å] and angles [°] for $[Zn_4(OH)_2(NCO)_2(pko)_4]\cdot 3DMF\cdot H_2O$ (**3**·3DMF·H_2O).[a]

Zn(1)···Zn(2)	3.316(1)	Zn(1)–N(21)	1.918(7)
Zn(1)···Zn(2′)	3.313(1)	Zn(2)–O(31)	2.122(4)
Zn(1)···Zn(1′)	5.788(1)	Zn(2)–O(31′)	2.104(4)
Zn(2)···Zn(2′)	3.233(1)	Zn(2)–N(1)	2.188(6)
Zn(1)–O(1)	1.966(5)	Zn(2)–N(11)	2.163(6)
Zn(1)–O(11′)	1.946(5)	Zn(2)–N(2)	2.130(5)
Zn(1)–O(31)	1.962(4)	Zn(2)–N(12)	2.151(5)
O(1)–Zn(1)–O(11′)	101.6(2)	N(2)–Zn(2)–N(12)	159.9(2)
O(31)–Zn(1)–N(21)	122.2(3)	Zn(1)–O(31)–Zn(2)	108.5(2)
O(31)–Zn(2)–N(1)	160.0(2)	Zn(1)–O(31)–Zn(2′)	109.1(2)
O(31′)–Zn(2)–N(11)	159.6(2)	Zn(2)–O(31)–Zn(2′)	99.8(2)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x* + 2, –*y* + 1, –*z*.

Table 4. Selected interatomic distances [Å] and angles [°] for $[Zn_4(OH)_2(acac)_2(pko)_4]\cdot 4CH_2Cl_2$ (**4**·$4CH_2Cl_2$).[a]

Zn(1)···Zn(2)	3.433(1)	Zn(2)–O(42)	2.062(5)
Zn(1)···Zn(2′)	3.467(1)	Zn(1)–O(31)	2.066(6)
Zn(1)···Zn(1′)	3.164(1)	Zn(1)–O(31′)	2.051(6)
Zn(2)···Zn(2′)	6.132(1)	Zn(1)–N(1)	2.192(6)
Zn(2)–O(1)	1.983(5)	Zn(1)–N(11)	2.208(6)
Zn(2)–O(11′)	2.005(5)	Zn(1)–N(2)	2.166(6)
Zn(2)–O(31)	2.082(5)	Zn(1)–N(12)	2.163(5)
Zn(2)–O(41)	2.007(6)		
O(1)–Zn(2)–O(31)	97.3(2)	O(31′)–Zn(1)–N(11)	158.2(2)
O(1)–Zn(2)–O(42)	91.3(2)	N(2)–Zn(1)–N(12)	154.0(2)
O(31)–Zn(2)–O(42)	168.3(2)	Zn(2)–O(31)–Zn(1)	111.7(3)
O(41)–Zn(2)–O(42)	87.7(2)	Zn(2)–O(31)–Zn(1′)	114.1(3)
O(31)–Zn(1)–N(1)	159.9(2)	Zn(1)–O(31)–Zn(1′)	100.4(2)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation –*x* + 2, –*y* + 1, –*z* + 1.

is evidence for an additional weak interaction between Zn(1) and Zn(1′), and the "free" benzoate oxygen atoms O(32) and O(32′), which generates an asymmetric chelating carboxylate group. Further support for this structural assignment comes from the coordination environment around Zn(1), which is very distorted from tetrahedral geometry; thus, an alternative description for the Zn(1) polyhedron is as an edge-capped tetrahedron.

The separations between neighbouring metal ions in **1** [3.315(1), 3.334(1) Å] are significantly shorter than those observed in regular 12-MC-4 complexes [M···M distances are approx. 4.6 Å].[15,18,19,21a] If we consider that, in the inverse 12-MC-4 compounds, the M···M separation is the bite distance, then this separation is longer than the O···O distance in regular MCs (ca. 2.6 Å) which is considered as the bite distance.

Complex **1** is only the second structurally characterised example of a tetranuclear zinc(II) benzoate cluster, the first being $[Zn_4O(O_2CPh)_6]$.[40]

The molecular structures of **2**·4DMF, **3**·3DMF·H_2O and **4**·$4CH_2Cl_2$ are similar to the structure of **1**·3MeCN except that the two terminal $PhCO_2^-$ ligands of **1** are replaced by two monodentate azido (**2**·4DMF), two monodentate isocyanato (i.e. *N*-bonded, **3**·3DMF·H_2O) or two bidentate chelating acetylacetonate groups (**4**·$4CH_2Cl_2$). Due to the presence of the purely monodentate N_3^- and NCO^- ligands in **2**·4DMF and **3**·3DMF·H_2O, respectively, instead of the anisobidentate benzoate ligands in **1**·3MeCN, the coordination environments of the tetrahedral Zn ions are less distorted; the angles around these metal ions in **2**·4DMF and **3**·3DMF·H_2O are in the ranges 102.0(1)–119.5(2)° and 101.6(2)–122.2(3)°, respectively [vs. the 100.9(3)–133.3(2)° range observed in **1**·3MeCN]. The presence of the chelating $acac^-$ ligands in **4**·$4CH_2Cl_2$ creates a truly five-coordination at two metal ions [Zn(2) and Zn(2′) in Figure 5]. The five donor atoms around Zn(2) [and Zn(2′)] do not create a regular polyhedron. Analysis of the shape-determining angles using the approach of Reedijk and coworkers[41] yields a value for the trigonality index, τ, of 0.61 (τ = 0 and 1 for perfect square-pyramidal (spy) and trigonal-bipyramidal (tbp) geometries, respectively). Thus, the geometry about Zn(2) is significantly distorted and can better be described as distorted tbp. With use of this description, the axial sites of Zn(2) are occupied by atoms O(31) and O(42) with atoms O(1), O(11′) and O(41) making up the equatorial plane (Figure 4 and Table 3).

The $Zn–N_{azido}$ [1.925(5) Å] and $Zn–N_{isocyanato}$ [1.918(7) Å] bond lengths in **2**·4DMF and **3**·3DMF·H_2O, respectively, are typical for such terminal bonds in tetrahedral zinc(II) complexes. For comparison, the $Zn–N_{azido}$ bond lengths in $[Zn(N_3)_2(py)_2]$ (py = pyridine)[42] are 1.928(16) and 1.945(17) Å, while the $Zn–N_{isocyanato}$ bond lengths in $[Zn(NCO)_2(4\text{-dmap})_2]$, where 4-dmap is 4-(dimethylamino)pyridine, are 1.909(5) and 1.942(5) Å. The azido and isocyanato ligands are almost linear [N(21)–N(22)–N(23) = 175.8(12)°, N(21)–C(41)–O(21) = 176(2)°]; these ligands are coordinated in a bent (N_3^-) or slightly bent (NCO^-) fashion as indicated by the Zn–N–N [134.0(7)°] and Zn–N–C [160.7(10)°] angles, respectively (Table 4).

The benzoate cluster **1** has a similar structure to its acetate version,[24a] while the molecular structures of the pseudohalide inverse 12-MC-4 complexes **2** and **3** are also very similar to the structure of the halide analogue $[Zn_4(OH)_2Cl_2(pko)_4]$.[24b] Obviously, the replacement of $MeCO_2^-$ by $PhCO_2^-$, and of Cl^- by N_3^- and NCO^- has little structural effect. Rather than discuss similarities, we list in Table 5 comparative structural parameters for the $\{(OH)_2[\text{inv}12\text{-}MC_{Zn^{II}N(pko)}\text{-}4]X_2\}$ complexes (X = Cl, N_3, NCO). The remarkable similarity of the molecular structures of the three complexes is clearly evident. The presence of the two five-coordinate Zn anions in **4** {instead of two four-coordinate Zn ions in $[Zn_4(OH)_2Cl_2(pko)_4]$, **2** and **3**} has few slight structural consequences. The $Zn_{five\text{-}coord}–O_{hydroxo}$ [2.082(5) Å] and $Zn_{five\text{-}coord}–O_{oximate}$ [mean value: 1.994(5) Å] bond lengths are longer than the corresponding $Zn_{tetr}–O_{hydroxo}$ and mean $Zn_{tetr}–O_{oximate}$ ones (Table 5), as expected. The $Zn_{five\text{-}coord}\cdots Zn_{five\text{-}coord}$ separation [6.132(1) Å] is longer than the $Zn_{tetr}\cdots Zn_{tetr}$ ones (Table 5), whereas the $Zn_{oct}\cdots Zn_{oct}$ interatomic distance [3.164(1) Å] and the mean $Zn_{oct}–O_{hydroxo}$ bond length [2.059(6) Å] are shorter than the corresponding distances in $\{(OH)_2[\text{inv}12\text{-}MC_{Zn^{II}N(pko)}\text{-}4]X_2\}$ (X = Cl, N_3, NCO).

Table 5. Selected, comparative structural data for the halide/pseudohalide inverse 12-MC-4 complexes $[Zn_4(OH)_2Cl_2(pko)_4]$, $[Zn_4(OH)_2(N_3)_2(pko)_4]$ (**2**) and $[Zn_4(OH)_2(NCO)_2(pko)_4]$ (**3**).

Parameter [Å or °]	$[Zn_4(OH)_2Cl_2(pko)_4]$	**2**	**3**
$Zn_{tetr}\cdots Zn_{tetr}$	5.826	5.763	5.788
$Zn_{oct}\cdots Zn_{oct}$	3.231	3.243	3.233
$Zn_{tetr}\cdots Zn_{oct}$[a]	3.326	3.307	3.315
$Zn_{tetr}–O_{hydroxo}$	1.963	1.953	1.962
$Zn_{tetr}–O_{oximate}$[a]	1.960	1.965	1.956
$Zn_{oct}–O_{hydroxo}$[a]	2.118	2.113	2.113
$Zn_{oct}–N_{pyridyl}$[a]	2.178	2.183	2.176
$Zn_{oct}–N_{oximate}$[a]	2.144	2.149	2.141
$Zn_{tetr}–O_{hydroxo}–Zn_{oct}$[a]	109.4	108.8	108.8
$Zn_{oct}–O_{hydroxo}–Zn_{oct}$	99.4	100.3	99.8
$\Sigma(Zn–O_{hydroxo}–Zn)$	318.1	317.9	317.4

[a] Mean value.

$[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]\cdot 2.5H_2O\cdot 1.5MeOH$ ($5\cdot 2.5H_2O\cdot 1.5MeOH$) and $[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]\cdot 2.5H_2O\cdot MeOH$ ($6\cdot 2.5H_2O\cdot MeOH$)

Fully or partially labelled plots of the cations and anions present in compounds **5**·$2.5H_2O$·1.5MeOH and **6**·$2.5H_2O$·MeOH, are shown in Figures 6, 7, 8, and 9. Selected interatomic distances and angles are listed in Tables 6, 7, 8, and 9. The molecular structures of the pentanuclear cations $[Zn_5Cl_2(pko)_6]^{2+}$ and $[Zn_5(NCS)_2(pko)_6(MeOH)]^{2+}$ are similar in many aspects and, thus, only the structure of the chloride-containing cation will be described in detail.

Complex **5**·$2.5H_2O$·1.5MeOH crystallises in the triclinic space group $P\bar{1}$. Its structure consists of the pentanuclear $[Zn_5Cl_2(pko)_6]^{2+}$ cation, the novel $[ZnCl(NCS)_3]^{2-}$ anion, and solvate H_2O and MeOH molecules; the solvate molecules will not be further discussed. The five Zn ions of the cation are held together by six pko^- ligands which adopt three different coordination modes. Two pko^- ligands adopt the coordination mode 2.1110, two are in the rare 3.1111 fashion, while the rest behave as 3.2111 ligands (see Figure 1). The five metal ions define two nearly equilateral triangles sharing a common apex at Zn(1). The "central" Zn(1) ion is in a distorted $O_2(N_{pyridyl})_2(N_{oximate})_2$ *cis-trans-cis* octahedral environment. Zn(2) and Zn(3) are bound to an $O_2(N_{pyridyl})_2(N_{oximate})$ set of donor atoms, while Zn(4) and Zn(5) are bound to an $O(N_{pyridyl})_2(N_{oximate})Cl$ set. The

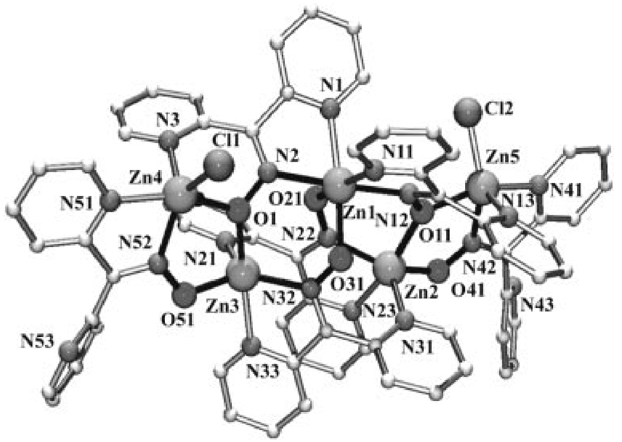


Figure 6. Partially labeled POV-RAY plot of the pentanuclear cation $[Zn_5Cl_2(pko)_6]^{2+}$ of the complex **5**·2.5H_2O·1.5MeOH.

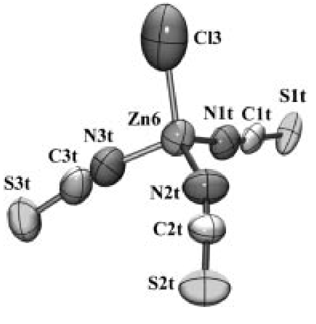


Figure 7. Structure of the anion $[ZnCl(NCS)_3]^{2-}$ of complex **5**·2.5H_2O·1.5MeOH.

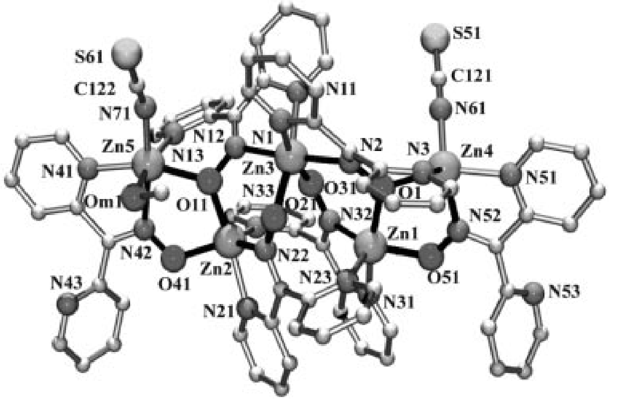


Figure 8. Partially labeled POV-RAY plot of the pentanuclear cation $[Zn_5(NCS)_2(pko)_6(MeOH)]^{2+}$ of complex **6**·2.5H_2O·MeOH.

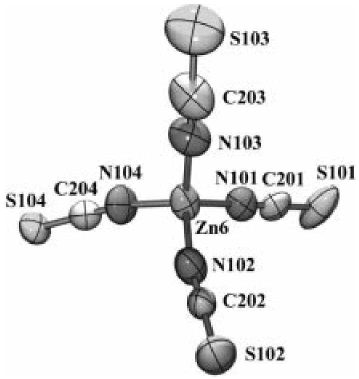


Figure 9. Structure of the anion $[Zn(NCS)_4]^{2-}$ of complex **6**·2.5H_2O·MeOH.

Table 6. Selected interatomic distances [Å] and angles [°] for the cation $[Zn_5Cl_2(pko)_6]^{2+}$ present in complex **5**·2.5H_2O·1.5MeOH.

Zn(1)···Zn(2)	3.767(1)	Zn(2)–N(23)	2.159(7)
Zn(1)···Zn(3)	3.756(1)	Zn(2)–N(31)	2.064(6)
Zn(1)···Zn(4)	4.902(1)	Zn(2)–N(22)	2.073(6)
Zn(1)···Zn(5)	4.896(1)	Zn(3)–O(1)	2.063(5)
Zn(2)···Zn(3)	4.820(1)	Zn(3)–O(51)	1.968(5)
Zn(2)···Zn(4)	7.776(1)	Zn(3)–N(21)	2.091(6)
Zn(2)···Zn(5)	3.627(1)	Zn(3)–N(33)	2.167(7)
Zn(3)···Zn(4)	3.631(1)	Zn(3)–N(32)	2.078(6)
Zn(3)···Zn(5)	7.759(1)	Zn(4)–O(1)	2.089(5)
Zn(4)···Zn(5)	9.785(1)	Zn(4)–N(3)	2.107(7)
Zn(1)–O(21)	2.065(5)	Zn(4)–N(51)	2.089(7)
Zn(1)–O(31)	2.048(5)	Zn(4)–N(52)	2.109(7)
Zn(1)–N(1)	2.152(7)	Zn(4)–Cl(1)	2.232(3)
Zn(1)–N(11)	2.168(7)	Zn(5)–O(11)	2.081(5)
Zn(1)–N(2)	2.138(6)	Zn(5)–N(13)	2.088(7)
Zn(1)–N(12)	2.112(6)	Zn(5)–N(41)	2.078(7)
Zn(2)–O(11)	2.077(6)	Zn(5)–N(42)	2.114(8)
Zn(2)–O(41)	1.973(5)	Zn(5)–Cl(2)	2.169(5)
O(21)–Zn(1)–N(11)	172.2(2)	N(21)–Zn(3)–N(32)	119.7(2)
O(31)–Zn(1)–N(1)	173.4(2)	O(1)–Zn(4)–N(3)	82.7(2)
N(2)–Zn(1)–N(12)	176.6(3)	O(1)–Zn(4)–N(51)	157.9(3)
O(11)–Zn(2)–N(23)	163.9(2)	N(52)–Zn(4)–Cl(1)	137.5(2)
O(41)–Zn(2)–N(23)	88.3(2)	O(11)–Zn(5)–N(41)	159.8(3)
N(31)–Zn(2)–N(22)	119.5(2)	N(13)–Zn(5)–N(41)	100.7(3)
O(1)–Zn(3)–N(21)	95.9(2)	N(42)–Zn(5)–Cl(2)	136.9(2)
O(1)–Zn(3)–N(33)	166.0(2)		

Table 7. Selected bond lengths [Å] and angles [°] for the anion $[ZnCl(NCS)_3]^{2-}$ present in complex **5**·2.5H_2O·1.5MeOH.

Zn(6)–Cl(3)	2.334(10)	Zn(6)–N(2t)	1.933(13)
Zn(6)–N(1t)	1.916(13)	Zn(6)–N(3t)	1.90(2)
Cl(3)–Zn(6)–N(1t)	111.0(4)	N(1t)–Zn(6)–N(2t)	110.7(5)
Cl(3)–Zn(6)–N(2t)	111.0(4)	N(1t)–Zn(6)–N(3t)	111.7(6)
Cl(3)–Zn(6)–N(3t)	106.1(5)	N(2t)–Zn(6)–N(3t)	106.2(6)

five donor atoms around Zn(2) and Zn(3) create a very distorted polyhedron. The τ values[41] for Zn(2) and Zn(3) are 0.48 and 0.54, respectively. We prefer to describe the geometry about these metal ions as very distorted tbp. With use of this description, the axial sites of Zn(2) are occupied by atoms O(11) and N(23), while those of Zn(3) by atoms O(1) and N(33). The Zn(4) and Zn(5) coordination geometries are better described as very distorted spy with the 2-pyridyl nitrogenatoms N(3) and N(13) occupying the apical positions for Zn(4) and Zn(5), respectively; The τ values[41] are 0.34 [Zn(4)] and 0.38 [Zn(5)]. The Zn(1)–$N_{pyridyl}$ and Zn(1)–$N_{oximate}$ bonds are slightly longer than the corresponding Zn(2,3,4,5)–N bonds, consistent with the higher coordination number for Zn(1). The novel Zn_5 topology in the cation of **5** could have been described as two 9-MC-3 rings fused at Zn(1) if the Zn(3)–O(1) and Zn(2)–O(11) bonds were absent. In this case, however, the Zn(3) and Zn(2) ions reach across their respective 9-MC-3 rings and bind to the oxime oxygen atoms of the opposite pko^- li-

Table 8. Selected interatomic distances [Å] and angles [°] for the cation $[Zn_5(NCS)_2(pko)_6]^{2+}$ present in complex **6**·$2.5H_2O$·MeOH

Zn(1)···Zn(2)	4.793(1)	Zn(2)–N(22)	2.096(4)
Zn(1)···Zn(3)	3.750(1)	Zn(3)–O(21)	2.083(4)
Zn(1)···Zn(4)	3.622(1)	Zn(3)–O(31)	2.038(3)
Zn(1)···Zn(5)	7.710(1)	Zn(3)–N(1)	2.148(4)
Zn(2)···Zn(3)	3.725(1)	Zn(3)–N(11)	2.217(5)
Zn(2)···Zn(4)	7.790(1)	Zn(3)–N(2)	2.166(4)
Zn(2)···Zn(5)	3.587(1)	Zn(3)–N(12)	2.130(4)
Zn(3)···Zn(4)	4.995(1)	Zn(4)–O(1)	2.102(4)
Zn(3)···Zn(5)	4.853(1)	Zn(4)–N(3)	2.091(5)
Zn(4)···Zn(5)	9.829(2)	Zn(4)–N(51)	2.124(5)
Zn(1)–O(1)	2.057(4)	Zn(4)–N(52)	2.089(5)
Zn(1)–O(51)	1.971(4)	Zn(4)–N(61)	1.959(6)
Zn(1)–N(23)	2.064(5)	Zn(5)–O(11)	2.071(4)
Zn(1)–N(31)	2.149(5)	Zn(5)–Om(1)	2.205(4)
Zn(1)–N(32)	2.083(4)	Zn(5)–N(13)	2.183(4)
Zn(2)–O(11)	2.036(4)	Zn(5)–N(41)	2.110(5)
Zn(2)–O(41)	1.986(4)	Zn(5)–N(42)	2.177(5)
Zn(2)–N(21)	2.171(5)	Zn(5)–N(71)	2.020(6)
Zn(2)–N(33)	2.087(4)		
O(1)–Zn(1)–N(31)	162.1(2)	O(1)–Zn(4)–N(51)	158.7(2)
O(51)–Zn(1)–N(32)	134.8(2)	O(1)–Zn(4)–N(61)	96.6(2)
N(23)–Zn(1)–N(31)	101.9(2)	N(3)–Zn(4)–N(51)	99.5(2)
O(11)–Zn(2)–N(21)	166.7(2)	N(3)–Zn(4)–N(52)	113.1(2)
O(41)–Zn(2)–N(22)	131.3(2)	N(3)–Zn(4)–N(61)	114.8(2)
N(21)–Zn(2)–N(33)	92.3(2)	O(11)–Zn(5)–N(41)	157.0(2)
O(21)–Zn(3)–N(11)	170.1(2)	Om(1)–Zn(5)–N(13)	168.5(2)
O(31)–Zn(3)–N(1)	168.9(2)	N(42)–Zn(5)–N(71)	169.0(2)
N(2)–Zn(3)–N(12)	176.0(2)		

Table 9. Selected bond lengths [Å] and angles [°] for the anion $[Zn(NCS)_4]^{2-}$ present in complex **6**·$2.5H_2O$·MeOH.

Zn(6)–N(101)	1.960(10)	Zn(6)–N(103)	1.925(11)
Zn(6)–N(102)	1.962(9)	Zn(6)–N(104)	1.922(9)
N(101)–Zn(6)–N(102)	109.1(4)	N(102)–Zn(6)–N(103)	105.8(4)
N(101)–Zn(6)–N(103)	109.8(4)	N(102)–Zn(6)–N(104)	109.6(4)
N(101)–Zn(6)–N(104)	111.8(4)	N(103)–Zn(6)–N(104)	110.7(5)

gands. This causes two "collapsed"[4,18] 9-metallacrown-3 structures sharing a common apex at Zn(1). Each "collapsed" structure is essentially a cation-vacant metallacrown.

Besides the pentanuclear cation, the structure contains a novel (from the chemical composition viewpoint) chlorotris(isothiocyanato)zincate(2–) anion (Figure 7). Three NCS^- ions coordinating through their nitrogen atoms and one terminal chloro ligand surround Zn(6). The bond angles about the metal ion are in the range 106.1(5)–111.7(6)°, and show a slight distortion of the ZnN_3Cl tetrahedron. The three isothiocyanate groups bind the zinc ion in a virtually linear fashion, with the C–N–Zn bond angles in the range of 158.2(13)–171.3(11)°.

The molecular structure of the pentanuclear cation of **6**·$2.5H_2O$·MeOH is similar to the structure of the cation of **5**·$2.5H_2O$·1.5MeOH except that the two terminal chloro ligands of the latter are replaced by two terminal isothiocyanato ligands in the former and one of the five-coordinate metal ions of **5**·$2.5H_2O$·1.5MeOH [Zn(5) in Figure 6] has become six-coordinate in **6**·$2.5H_2O$·MeOH [Zn(5) in Figure 8] through coordination of one terminal MeOH ligand. Again, the five metal ions define two nearly equilateral triangles sharing a common apex [at Zn(3)], the six pko^- ligands adopt three different coordination modes (2.1110, 3.1111, 3.2111, see Figure 1) and the Zn_5 topology can be described as two fused "collapsed" 9-MC-3 rings [in this case the Zn(2) and Zn(1) ions reach across their respective 9-MC-3 rings and bind to the oxime oxygen atoms O(11) and O(1) of the opposite pko^- ligands]. Another slightly different structural feature of **6**·$2.5H_2O$·MeOH is worthy of comment. In **5**·$2.5H_2O$·1.5MeOH the two five-coordinate, chloride-bound metal ions [Zn(4) and Zn(5) in Figure 6] have a distorted spy coordination environment, whereas the polyhedron of the unique five-coordinate, isothiocyanate-bound metal ion [Zn(4) in Figure 8] in **6**·$2.5H_2O$·MeOH is better described as a very distorted trigonal bipyramid (τ = 0.45) with atoms O(1) and N(51) occupying the axial sites. The $Zn(4)–N_{isothiocyanate}$ bond [1.959(6) Å] is shorter than the $Zn(5)–N_{isothiocyanate}$ bond [2.020(6) Å], which is consistent with the lower coordination number for Zn(4) [five vs. six for Zn(5)] (Table 8).

Besides the pentanuclear cation, the structure contains a tetraisothiocyanatozincate(2–) anion (Figure 9). Four NCS^- anions almost equivalently surround Zn(6), coordinating through the nitrogen atoms such that a slightly distorted tetrahedral geometry occurs. The Zn–N bond lengths [1.922(9)–1.962(9) Å] and N–Zn–N bond angles [105.8(4)–111.8(4)°] are typical for complexes containing the $[Zn(NCS)_4]^{2-}$ anion.[45] All the NCS^- groups bind the metal ion in a virtually linear fashion, with the C–N–Zn bond angles in the range 168.4(10)–175.4(9)° (Table 9).

The cations present in compounds **5** and **6** represent the third and fourth, respectively, structurally characterised examples of non-organometallic, pentanuclear Zn^{II} complexes with *O,N* ligation (there are several examples with S-, Te- or P-containing ligands). The other two examples are $[\{Zn_2L(O_2CMe)_2\}_2Zn(H_2O)_4]$[46a] and $[Zn_5(poap\text{-}H)_6](ClO_4)_4$,[46b] where L is the trianion of a Schiff base derived from glycine and poap-H the monoanion of an alkoxydiazine polydentate ligand.

A remarkable structural feature of complexes **5** and **6** is the presence of pko^- ligands that adopt three different coordination modes. Since most complexes containing *bridging* pko^- ligands have been reported only recently, we felt it timely to collect all metal complexes of bridging pko^- ligands in Table 10, together with the pko^- coordination modes for convenient comparison. Inspection of Table 10 clearly shows that the 2.1110 ligation mode (Figure 1) is the most common one and that only two previously characterised clusters, namely $[Ni_4(pko)_6(MeOH)_2](OH)(ClO_4)$[26a] and $[Zn_8(shi)_4(pko)_4(MeOH)_2]$,[26b] contain di-2-pyridyl ketone oximate(1–) ligands exhibiting two different coordination modes; thus, the cations of **5** and **6** are unique in exhibiting three different coordination modes of the pko^- ligands.

IR Spectra

The IR spectra of **1**, **2**·4DMF and **4** exhibit a medium band at 3414–3386 cm^{-1} assignable[47a] to $\nu(OH)_{OH^-}$. The

Table 10. Structurally characterised complexes containing *bridging* pko$^-$ ligands.

Complex[a]	Coordination mode[b] of pko$^-$	Ref.
$[Ni_4(pko)_6(MeOH)_2]^{2+}$	2.1110, 2.1111	[26a]
$[M_3(pko)_6(CO)_8]$	2.1110	[37]
$[Ru_2(pko)_2(CO)_4]$	2.1110	[37]
$[Os_3(\mu\text{-}H)(pko)(CO)_9]$	2.1110	[37]
$[Mn_{12}O_6(OH)_4(OMe)_2(pko)_{12}]^{4+}$	2.1110	[17]
$[Mn_4(O_2CR)_2X_2(pko)_2\{(py)_2CO_2\}_2]$	2.1110	[27e]
$[Mn_3(OMe)_2Y_2(pko)_4]$	2.1110	[26b,26c]
$Zn_4(OH)_2Cl_2(pko)_4]$	2.1110	[24b]
$[Zn_8(shi)_4(pko)_4(MeOH)_2]$	2.1110, 3.1111	[24b]
$[Mn_4O(3,4\text{-}D)_4(pko)_4]$	2.1110	[26d]
$[Ni_4(NCS)_2(Hshi)_2(pko)_2(DMF)(MeOH)]$	2.1111	[18]
$[Ni_5(O_2CMe)_2(shi)_2(pko)_2]$	3.2111	[18]
$[Ni_{10}(MCPA)_2(shi)_5(pko)_3(MeOH)(H_2O)]$	3.2111	[18,23b]
$[Mn_2Ni_2(O_2CMe)_2(shi)_2(pko)_2(DMF)_5]$	2.1110	[18]
$[Zn_4(OH)_2(O_2CMe)_2(pko)_4]$	2.1110	[24a]
$[Cu_2(pko)_4]$[c]	2.1110	[44]
$[Zn_4(OH)_2Z_2(pko)_4]$	2.1110	this work
$[Zn_5X'_2(pko)_6]^{2+}$	2.1110, 3.2111, 3.1111	this work

[a] Counterions and solvate molecules have been omitted; 3,4-D = the anion of 3,4-dichlorophenoxyacetic acid; Hshi = the dianion of salicylhydroxamic acid; MCPA = the anion of 2-methyl-4-chlorophenoxyacetic acid; $(py)_2CO_2$ = the dianion of the *gem*-diol form of di-2-pyridyl ketone; shi = the trianion of salicylhydroxamic acid; R = Me, Ph; X = Cl, Br; X′ = Cl, NCS; Y = NCS, Cl, NCO; Z = $PhCO_2$, N_3, NCO, acac. [b] Using Harris notation[16] (see also Figure 1). [c] This complex also contains N,N′-chelating, i.e., terminal, pko$^-$ ligands.

presence of both hydroxo ligands and water solvate molecules in **3**·3DMF·H_2O is manifested by a broad IR band of medium intensity at about 3400 cm^{-1}.[47b] The ν(OH) band in the spectra of the crystals of **5**·2.5H_2O·1.5MeOH and **6**·2.5H_2O·MeOH appears at 3330 and 3415 cm^{-1}, respectively. The presence of DMF in **2**·4DMF and **3**·3DMF·H_2O is manifested by a strong band at 1672–1665 cm^{-1} and a weak band at around 640 cm^{-1}, assigned to ν(C=O) and δ(OCN), respectively.[48] The absence of shifts of these bands in the complexes, when compared with the corresponding bands in the spectrum of free DMF,[48] confirms that there is no interaction between DMF and the Zn^{II} atoms.

Two bands, one strong at about 1595 cm^{-1} and one of variable intensity at about 1220 cm^{-1}, are common in the spectra of **1**–**6**; these bands are tentatively assigned to the oximate ν(C=N) and ν(N–O) vibrational modes,[24b] respectively, although the higher-wavenumber band may also have an aromatic stretch character.

The strong bands at 1566 and 1366 cm^{-1} in the spectrum of **1** are assigned to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes of the benzoate ligands, respectively;[49] the former may also involve a 2-pyridyl stretching character. The difference Δ [$\Delta = \nu_{as}(CO_2) - \nu_s(CO_2)$] is 200 cm^{-1}, more than that for NaO_2CPh (184 cm^{-1}), as expected for monodentate ligation.[49] In the spectrum of **4**, the bands at 1594 and 1518 cm^{-1} certainly involve a $\nu(C\cdots C)_{acac^-}$ [coupled with $\nu(C\cdots O)_{acac^-}$] character and a $\nu(C\cdots O)_{acac^-}$ [coupled with $\nu(C\text{–}C)_{acac^-}$] character, respectively;[50] however, overlap with other modes renders exact assignments difficult. The spectrum of **2**·4DMF exhibits an intense band at 2070 cm^{-1}, assigned to the asymmetric stretching mode of the azido ligands.[50] Similarly, the strong band at 2236 cm^{-1} in the spectrum of **3**·3DMF·H_2O is assigned to the $\nu_{as}(NCO)$ [consisting mainly of ν(CN)] vibrational mode of the isocyanato ligands.[50,51] The spectra of the dried samples **5**·2.5H_2O and **6**·2.5H_2O exhibit the ν(CN) mode at 2076 and 2074 cm^{-1}, respectively; These wavenumbers are typical of terminal isothiocyanato groups.[50] The existence of the isothiocyanato ligands at different Zn^{II} coordination environments (tetrahedral, trigonal-bipyramidal, octahedral) in **6** does not lead to two or three ν(CN) bands and, thus, the different environments cannot be differentiated by IR spectroscopy. The expected ν_s(NNN), δ(NNN) [**2**·4DMF], ν_s(NCO) [consisting mainly of ν(CO)], δ(NCO) [**3**·3DMF·H_2O], ν(CS) and δ(NCS) [**5**·2.5H_2O, **6**·2·5H_2O] bands could not be located because they are obscured by pko$^-$ absorptions.

Conclusions and Perspectives

The further use of di-2-pyridyl ketone oxime in Zn chemistry has provided access to six new clusters, four tetranuclear and two pentanuclear. Complexes **1**–**4** are valuable additions to the small, but growing, family of inverse metallacrown complexes. The present work also extends the body of results that emphasise the ability of the monoanionic ligand pko$^-$ to form new structural types in 3d-metal chemistry. Complexes **5** and **6** are rare examples of pentanuclear zinc complexes with ligands containing N- and/or O-donors. Moreover the "collapsed" double, fused 9-metallacrown-3 structural type observed in these clusters is novel. The structural diversity displayed by the reported complexes stems from the coordinating versatility of pko$^-$ and its ability to exhibit two or even three distinct coordination modes in the same compound. The general structure of **5** and **6** is distinctly different from that of **2**, **3** and $[Zn_4(OH)_2Cl_2(pko)_4]$[24b] (these three complexes also have terminal pseudohalide or chloride ligands like **5** and **6**) emphasising the dependence of the product identity on the charge of the complex (neutral vs. cationic).

The isothiocyanate analogue of compounds **2** and **3** is not known, at least to date, and it is currently not evident whether the preparation and stability of the neutral $[Zn_4(OH)_2X_2(pko)_4]$ clusters are dependent on the particular nature of the pseudohalide ligand. Work is in progress to clarify this matter, and the use of $SeCN^-$ and $N(CN)_2^-$ is planned. The $PhCO_2^-$, N_3^-, NCO^- and $acac^-$ terminal ligands present in **1**–**4** could have future utility as sites for facile incorporation of other monodentate/bidentate ligands by metathesis, or as a means to access higher-nuclearity neutral or cationic Zn clusters using bis(monodentate)/bis(bidentate) bridging ligands, including aromatic heterocycles and dicarboxylates.

Results at the time of writing reveal that the nature of pko^- makes it a versatile ligand for a variety of objectives/advantages, including μ_3 behaviour, high-nuclearity cluster formation with a variety of 3d-, 4d- and 5d-metals, linking of clusters into polymeric arrays, 3d-4f mixed-metal chemistry and ferromagnetic exchange interactions. Clearly, the use of other polypyridyl oximes offers a potential route to other new clusters, and such studies – already well advanced – will be reported in due course.

Experimental Section

Materials and Physical Measurements: All manipulations were performed under aerobic conditions using materials and most solvents as received. DMF and MeOH were distilled from CaH_2 and Mg, respectively; they were both stored over molecular sieves (3 Å). $Zn(O_2CPh)_2\cdot 2H_2O$ was prepared by the reaction of $Zn(O_2CMe)_2\cdot 2H_2O$ with an excess of $PhCO_2H$ in $CHCl_3$ under reflux. C, H and N elemental analyses were performed with Perkin–Elmer 240B and EA 108 Carlo Erba analyzers. Zn was determined for some complexes by atomic absorption with a Perkin–Elmer 1100B spectrophotometer. IR spectra were recorded with Perkin–Elmer PC 16 and 1650 FT-IR spectrometers with samples prepared as KBr pellets.

$[Zn_4(OH)_2(O_2CPh)_2(pko)_4]\cdot 3MeCN$ (1·3MeCN) or $\{(OH)_2[inv12\text{-}MC_{Zn^{II}N(pko)}\text{-}4](O_2CPh)_2\}\cdot 3MeCN$: Treatment of a stirred, colourless solution of Hpko (0.120 g, 0.60 mmol) in MeCN (20 mL) with Et_3N (0.100 mL, 0.72 mmol) resulted in a pale-yellow solution. Solid $Zn(O_2CPh)_2\cdot 2H_2O$ (0.207 g, 0.60 mmol) was slowly added to this solution and it soon dissolved to give an essentially colourless solution. The filtered solution was allowed to slowly concentrate by solvent evaporation at room temperature for a period of 3–4 d. Well-formed colourless cubes appeared which were collected by filtration, washed with ice-cold MeCN (5 mL) and Et_2O (2.5 mL), and dried in air. Yield (based on the oxime): 0.130 g (65%). The dried solid was analysed as MeCN-free **1**. $C_{58}H_{44}N_{12}O_{10}Zn_4$ (1330.7): calcd. C 52.35, H 3.34, N 12.63; found C 52.51, H 3.40, N 12.49. The obtained crystals were good diffractors of X-rays, as long as they were kept in contact with the mother liquor to prevent solvent loss. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3414 cm^{-1} (m, broad), 1596 (s), 1566 (s), 1366 (s) 1214 (m) cm^{-1}.

$[Zn_4(OH)_2(N_3)_2(pko)_4]\cdot 4DMF$ (2·4DMF) or $\{(OH)_2[inv12\text{-}MC_{Zn^{II}N(pko)}\text{-}4](N_3)_2\}\cdot 4DMF$: a solution of NaN_3 (0.065 g, 1.00 mmol), Hpko (0.398 g, 2.00 mmol) and NaOH (0.080 g, 2.00 mmol) in DMF (50 mL) was added to a stirred solution of $Zn(NO_3)_2\cdot 4H_2O$ (0.523 g, 2.00 mmol) in the same solvent (50 mL). The resulting colourless solution was stirred for 1 h, filtered and then allowed to very slowly concentrate at room temperature for a period of 15 d. X-ray quality colourless crystals formed, which were collected by filtration, washed with Et_2O (5 mL) and dried in air. Yield (based on the oxime): 0.51 g (70%). $C_{56}H_{62}N_{22}O_{10}Zn_4$ (1464.8): calcd. C 45.92, H 4.27, N 21.04, Zn 17.85; found C 46.10, H 4.17, N 19.44, Zn 18.80. The crystals of **2**·4DMF were found to be slightly hygroscopic, and they were kept in the mother liquor until a suitable crystal had been found for X-ray crystallography. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3386 cm^{-1} (m, broad), 2070 (s), 1672 (s), 1596 (s), 1218 (s), 640 (w) cm^{-1}.

$[Zn_4(OH)_2(NCO)_2(pko_4]\cdot 3DMF\cdot H_2O$ (3·3DMF·H₂O) or $\{(OH)_2[inv12\text{-}MC_{Zn^{II}N(pko)}\text{-}4](NCO)_2\}\cdot 3DMF\cdot H_2O$: A solution of NaOCN (0.065 g, 1.00 mmol), Hpko (0.398 g, 2.00 mmol) and NaOH (0.080 g, 2.00 mmol) in MeOH (50 mL) was added to a stirred solution of $ZnCl_2$ (0.273 g, 2.00 mmol) in the same solvent (50 mL). The resulting solution was stirred vigorously for about 1 h, filtered and then DMF (50 mL) was added. The new colourless solution obtained was allowed to concentrate by solvent evaporation at room temperature for about 10 d. Well-formed colourless crystals appeared, which were collected by filtration, washed with Et_2O (2 × 3 mL) and dried in air. Yields (based on the oxime) as high as 0.48 g (68%) were obtained. $C_{55}H_{57}N_{17}O_{12}Zn_4$ (1409.65): calcd. C 46.86, H 4.08, N 16.90, Zn 18.55; found C 47.10, H 3.73, N 16.85, Zn 19.06. The crystal selected for X-ray crystallography was kept in contact with the mother liquor to prevent H_2O loss. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3400 cm^{-1} (m, broad), 2236 (s), 1665 (s), 1595 (s), 1216 (s), 638 (w) cm^{-1}.

$[Zn_4(OH)_2(acac)_2(pko)_4]\cdot 4CH_2Cl_2$ (4·4CH₂Cl₂) or $\{(OH)_2[inv12\text{-}MC_{Zn^{II}N(pko)}\text{-}4](acac)_2\}\cdot 4CH_2Cl_2$: A solution of Hpko (0.040 g, 0.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a colourless slurry of $Zn(acac)_2\cdot H_2O$ (0.052 g, 0.18 mmol) in the same solvent (15 mL). No noticeable colour change occurred. The mixture was refluxed under vigorous stirring for 15–20 min, a small quantity of undissolved material was removed by filtration and the filtrate layered with Et_2O (20 mL). Slow mixing gave X-ray quality crystals of **4**·4CH₂Cl₂. The crystals were collected by filtration, washed with cold CH_2Cl_2 (5 mL) and Et_2O (2 × 5 mL) and dried in air. Yield (based on Zn^{II}): 0.036 g (63%). The dried solid was analysed as CH_2Cl_2-free **4**. $C_{54}H_{48}N_{12}O_{10}Zn_4$ (1286.7): calcd. C 50.40, H 3.77, N 13.07; found C 50.53, H 3.71, N 13.00. The obtained crystals were stable as long as they were kept in contact with the mother liquor to prevent CH_2Cl_2 loss. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3378 cm^{-1} (m, broad), 1594 (m), 1518 (s), 1222 (m) cm^{-1}.

$[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]\cdot 2.5H_2O\cdot 1.5MeOH$ (5·2.5H₂O·1.5MeOH) and $[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]\cdot 2.5H_2O\cdot MeOH$ (6·2.5H₂O·MeOH) as a Mixture: A solution of NaSCN (0.081 g, 1.00 mmol), Hpko (0.398 g, 2.00 mmol) and NaOH (0.080 g, 2.00 mmol) in MeOH (50 mL) was added to a stirred solution of $ZnCl_2$ (0.273 g, 2.00 mmol) also in MeOH (50 mL). The resulting colourless solution was stirred for 1 h and during this time its colour turned to pale yellow. The pale-yellow solution was filtered and allowed to slowly concentrate by solvent evaporation at room temperature. After several days, an approximately 1:3 mixture of colourless prisms and pale-yellow needles formed. The crystals were carefully collected by filtration. The two products were readily separable manually, and the colourless and pale-yellow crystals proved by single-crystal X-ray crystallography to be complexes **5**·2.5H₂O·1.5MeOH and **6**·2.5H₂O·MeOH, respectively. A batch of colourless crystals were used for analyses and IR spectroscopy. The dried (in air) sample was analysed as MeOH-free **5**·2.5H₂O.

$C_{69}H_{53}Cl_3N_{21}O_{8.5}S_3Zn_6$ (1907.2): calcd. C 43.45, H 2.81, N 15.43; found C 43.67, H 2.77, N 15.36. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3330 cm^{-1} (m, broad), 2076 (s), 1597 (s), 1214 (m) cm^{-1}.

[$Zn_5(NCS)_2(pko)_6(MeOH)$][$Zn(NCS)_4$]·2.5H_2O·MeOH (6·2.5H_2O·MeOH). Method A: A colourless solution of Hpko (0.060 g, 0.30 mmol) and NaSCN (0.024 g, 0.30 mmol) in MeOH (25 mL) was added to a colourless solution of $Zn(O_2CMe)_2·2H_2O$ (0.085 g, 0.39 mmol) in the same solvent (10 mL). The resulting pale-yellow solution was stirred for about 10 min and was then allowed to stand undisturbed in a closed flask at room temperature for 2 d. Well-formed pale-yellow crystals appeared, which were collected by filtration, washed with ice-cold MeOH (5 mL) and Et_2O (2 × 5 mL), and dried in air. Yield (based on the oxime): 0.083 g (83%). The crystals, which were kept in contact with the mother liquor to prevent MeOH loss, had identical unit-cell dimensions with those identified as **6**·2.5H_2O·MeOH in the above-mentioned experiment. The dried solid was analysed as MeOH-free **6**·2.5H_2O. $C_{73}H_{57}N_{24}O_{9.5}S_6Zn_6$ (2007.2): calcd. C 43.68, H 2.87, N 16.75; found C 44.32, H 2.86, N 16.51. Selected IR data (KBr pellet): $\tilde{\nu}$ = 3415 cm^{-1} (m, broad), 2074 (s), 1596 (s), 1216 (w) cm^{-1}. **Method B:** A suspension of compound **5**·2.5H_2O (0.191 g, 0.10 mmol) in warm MeOH/H_2O (40 mL, 10:1, v/v) was treated with an excess of NaSCN (0.041 g, 0.50 mmol). The mixture was stirred overnight at 45 °C, filtered to remove some undissolved starting material, and then allowed to stand undisturbed in closed vials at room temperature. Pale-yellow crystals formed within 12 h, and these were collected by filtration and washed with cold MeOH. Yield (based on **5**·2.5H_2O): 0.070 g (35%). The product was identified by microanalyses and IR comparison with material from method A.

X-ray Crystallographic Studies: Crystals of **1**·3MeCN, **2**·4DMF, **3**·3DMF·H_2O, **4**·4CH_2Cl_2, **5**·2.5H_2O·1.5MeOH and **6**·2.5H_2O·MeOH were mounted in capillaries filled with drops of mother liquor. Diffraction measurements for **1**·3MeCN, **2**·4DMF, **3**·3DMF·H_2O and **6**·2.5H_2O·MeOH were carried out with a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo-K_α radiation. The X-ray data sets for **4**·4CH_2Cl_2 and **5**·2.5H_2O·1.5MeOH were collected with a P2_1 Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu-K_a radiation. Complete crystal data and parameters for data collection and refinement are listed in Tables 11 and 12. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the ranges 11° < 2θ < 23° (for **1**·3MeCN, **2**·4DMF, **3**·3DMF·H_2O and **6**·2.5H_2O·MeOH) and 22° < 2θ < 54° (for **4**·4CH_2Cl_2 and **5**·2.5H_2O·1.5MeOH). Intensity data were recorded using the θ-2θ scan method. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarisation and Ψ-scan absorption (for **3**·3DMF·H_2O, **4**·4CH_2Cl_2, **5**·2.5H_2O·1.5MeOH and **6**·2.5H_2O·MeOH) corrections were applied using the Crystal Logic software package.

The structures were solved by direct methods using SHELXS-86[52a] and refined by full-matrix least-squares techniques on F^2 with SHELX-93[52b] (**1**·3MeCN, **4**·4CH_2Cl_2 and

Table 11. Crystal data and structure refinement for [$Zn_4(OH)_2(O_2CPh)_2(pko)_4$]·3MeCN (**1**·3MeCN), [$Zn_4(OH)_2(N_3)_2(pko)_4$]·4DMF (**2**·4DMF) and [$Zn_4(OH)_2(NCO)_2(pko_4)$]·3DMF·H_2O (**3**·3DMF·H_2O).

	1·3MeCN	**2**·4DMF	**3**·3DMF·H_2O
Empirical formula	$C_{64}H_{35}Zn_4N_{15}O_{10}$	$C_{56}H_{62}Zn_4N_{22}O_{10}$	$C_{55}H_{57}Zn_4N_{17}O_{12}$
Formula mass	1453.70	1464.76	1409.65
Colour and habit	colourless cubes	colourless prisms	colourless prisms
Crystal size [mm]	0.45 × 0.30 × 0.15	0.55 × 0.25 × 0.15	0.25 × 0.20 × 0.15
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a [Å]	12.108(6)	11.905(5)	11.886(5)
b [Å]	11.956(6)	17.660(6)	17.732(9)
c [Å]	13.251(6)	15.833(6)	15.812(7)
α [°]	67.39(2)	90	90
β [°]	83.02(2)	93.14(1)	92.53(1)
γ [°]	73.08(2)	90	90
V [$Å^3$]	1694(2)	3324(2)	3329(3)
Z	1	2	2
$\rho_{calcd.}$ [$g cm^{-3}$]	1.425	1.464	1.388
T [°C]	25	25	25
λ(Mo-K_a) [Å]	0.71073	0.71073	0.71073
μ [mm^{-1}]	1.466	1.497	1490
F(000)	742	1504	1444
2θ_{max} [°]	50.00	50.00	50.02
Index ranges	$-14 \leq h \leq 14$	$-14 \leq h \leq 13$	$-14 \leq h \leq 13$
	$-13 \leq k \leq 14$	$-21 \leq k \leq 0$	$0 \leq k \leq 21$
	$0 \leq l \leq 15$	$-18 \leq l \leq 0$	$0 \leq l \leq 18$
No. of reflections collected	6242	5586	5859
No. of indep. refl./$R_{int.}$	5958/0.0199	5384/0.0186	5584/0.0224
Data with $I > 2\sigma(I)$	4621	4062	4000
Parameters refined	495	465	398
$[\Delta/\sigma]_{max}$	0.023	0.003	0.003
GOF(on F^2)	1.058	1.095	1.083
R_1[a]	0.0486	0.0449	0.0728
wR_2[b]	0.1355	0.1134	0.2038
Residuals [$e Å^{-3}$]	0.517/–0.525	0.573/–0.545	0.985/–0.785

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

5·$2.5H_2O$·1.5MeOH) or SHELX-97[52c] (**2**·4DMF, **3**·3DMF·H_2O and **6**·$2.5H_2O$·MeOH). For **2**·4DMF almost all hydrogen atoms were located by difference maps and were refined isotropically, whereas for **3**·3DMF·H_2O, **5**·$2.5H_2O$·1.5MeOH and **6**·$2.5H_2O$·MeOH all hydrogen atoms were introduced at calculated positions as riding on their parent atoms. For **1**·3MeCN and **4**·$4CH_2Cl_2$ some hydrogen atoms were located by difference maps and were refined isotropically, and some were introduced at calculated positions as riding on bonded atoms. For example, in **4**·$4CH_2Cl_2$ all hydrogen atoms were located by difference maps and were refined isotropically, except those of the methyl groups of the acac$^–$ ligand which were introduced at calculated positions as riding on their parent carbon atoms. All non-hydrogen atoms of **4**·$4CH_2Cl_2$ were refined anisotropically. For the remaining structures, almost all non-hydrogen atoms were refined anisotropically. One of the solvate MeCN molecules of **1**·3MeCN was refined with occupation factor 0.50. For **2**·4DMF, one of the crystallographically independent solvate DMF molecules was refined isotropically; thus, no hydrogen atoms for that molecule were included. For **3**·3DMF·H_2O, one DMF and the H_2O solvate molecules were refined isotropically with occupation factors fixed to 10.5; no hydrogen atoms for these solvate molecules were included in the refinement. All the solvate molecules of **5**·$2.5H_2O$·1.5MeOH and the H_2O molecules of **6**·$2.5H_2O$·MeOH were refined isotropically. CCDC-254415 (**1**·3MeCN), -254416 (**2**·4DMF), -254417 (**3**·3DMF·H_2O), -254418 (**4**·$4CH_2Cl_2$), -254419 (**5**·$2.5H_2O$·1.5MeOH) and -254420 (**6**·$2.5H_2O$·MeOH) 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.

Acknowledgments

E. K., E. M.-Z. and S. P. P. thank the European Social Fund (ESF), the Operational Program for Educational and Vocational Training II (EPEAEK II) and particularly the Program PYTHAGORAS, for funding the above work. M. A., C. D.-S. and D. P. K. wish to thank The Greek General Secretariat for Research and Technology for the financial support of this research through PENED 2001/1034 Grant.

---

[1] M. Fujita, J. Y. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.

[2] H. Piotrowski, K. Polborn, G. Hilt, K. Severin, *J. Am. Chem. Soc.* **2001**, *123*, 2699–2700.

[3] a) J. J. Bodwin, V. L. Pecoraro, *Inorg. Chem.* **2000**, *39*, 3434–3435; b) M. Moon, I. Kim, M. S. Lah, *Inorg. Chem.* **2000**, *39*, 2710–2711.

[4] For an excellent review, see: V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwins-Ki, *Prog. Inorg. Chem.* **1997**, *45*, 83–177.

[5] a) A. J. Blake, R. O. Gould, P. E. Y. Milne, R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.* **1991**, 1453–1455; b) A. J. Blake,

Table 12. Crystal data and structure refinement for $[Zn_4(OH)_2(acac)_2(pko)_4]\cdot 4CH_2Cl_2$ (**4**·$4CH_2Cl_2$), $[Zn_5Cl_2(pko)_6][ZnCl(NCS)_3]\cdot 2.5H_2O\cdot 1.5MeOH$ (**5**·$2.5H_2O$·1.5MeOH) and $[Zn_5(NCS)_2(pko)_6(MeOH)][Zn(NCS)_4]\cdot 2.5H_2O\cdot MeOH$ (**6**·$2.5H_2O$·MeOH).

	4·$4CH_2Cl_2$	**5**·$2.5H_2O$·1.5MeOH	**6**·$2.5H_2O$·MeOH
Empirical formula	$C_{58}H_{56}Zn_4N_{12}O_{10}Cl_8$	$C_{70.5}H_{59}Zn_6N_{21}O_{10}S_3Cl_3$	$C_{74}H_{61}Zn_6N_{24}O_{10.5}S_6$
Formula mass	1626.22	1955.14	2039.05
Colour and habit	colourless plates	colourless prisms	pale yellow needles
Crystal size [mm]	0.35 × 0.15 × 0.08	0.08 × 0.14 × 0.30	0.22 × 0.34 × 0.70
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a [Å]	12.786(2)	18.552(3)	17.371(6)
b [Å]	13.439(2)	17.569(2)	30.14(1)
c [Å]	12.322(2)	16.493(2)	17.894(6)
α [°]	63.22(1)	105.87(1)	90
β [°]	67.19(1)	104.42(1)	103.65(1)
γ [°]	78.15(1)	105.50(1)	90
V [Å^3]	1741.2(5)	4672.4(11)	9105(5)
Z	1	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.551	1.390	1.487
T [°C]	25	25	25
λ(Mo-K_a) [Å]			0.71073
λ(Cu-K_a) [Å]	1.54180	1.54180	
μ [mm^{-1}]	4.907	3.614	1.760
F(000)	824	1976	4132
$2\theta_{max}$ [°]	124.90	102.08	45.60
Index ranges	$-13 \le h \le 11$	$-18 \le h \le 17$	$-18 \le h \le 18$
	$-13 \le k \le 14$	$-14 \le k \le 17$	$0 \le k \le 32$
	$0 \le l \le 13$	$0 \le l \le 16$	$-19 \le l \le 0$
No. of reflections collected	4728	10 307	12 767
No. of indep. refl./$R_{int.}$	4499/0.0580	9758/0.0328	12 311/0.0121
Data with $I > 2\sigma(I)$	3372	6712	9178
Parameters refined	488	1025	1098
$[\Delta/\sigma]_{max}$	0.013	0.009	0.013
GOF(on F^2)	1.061	1.052	1.072
R_1[a]	0.0723	0.0665	0.0468
wR_2[b]	0.1991	0.1838	0.1329
Residuals [e Å^{-3}]	1.058/–0.809	0.995/–0.516	0.882/–0.605

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

R. O. Gould, G. M. Grant, P. E. Y. Milne, D. Reed, R. E. P. Winpenny, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 195–197.

[6] a) S.-X. Liu, S. Lin, B.-Z. Lin, C.-C. Lin, J.-Q. Huang, *Angew. Chem. Int. Ed.* **2001**, *40*, 1084–1087; b) B. Kwak, H. Rhee, S. Park, M. S. Lah, *Inorg. Chem.* **1998**, *37*, 3599–3602.

[7] a) X. Yang, S. E. Johnson, S. I. Khan, M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 893–896; b) X. Yang, Z. Zheng, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1993**, *115*, 193–195; c) X. Yang, C. B. Knobler, Z. Zheng, M. F. Hawthorne, *J. Am. Chem. Soc.* **1994**, *116*, 7142–7159.

[8] a) R. W. Saalfrank, N. Löw, F. Hampel, H.-D. Stachel, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2209–2210; b) R. W. Saalfrank, N. Löw, S. Kareth, V. Seitz, F. Hampel, D. Stalke, M. Teichert, *Angew. Chem. Int. Ed.* **1998**, *37*, 172–175.

[9] a) E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67–137; b) J. A. Johnson, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2003**, *42*, 546–549; c) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, New York, **2000**, pp. 540–548.

[10] H. Rauter, E. C. Hillgeries, A. Erxleben, B. Lippert, *J. Am. Chem. Soc.* **1994**, *116*, 616–624.

[11] C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2003**, *42*, 3763–3766.

[12] P. J. Stang, K. Chen, *J. Am. Chem. Soc.* **1995**, *117*, 1667–1668.

[13] a) R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel, G. B. M. Vaughan, *Chem. Eur. J.* **2001**, *7*, 2765–2769; b) R. W. Saalfrank, C. Deutscher, H. Maid, A. M. Ako, S. Sperner, T. Nakajima, W. Bauer, F. Hampel, B. A. Hess, N. J. R. van Eikema Hommes, R. Puchta, F. W. Heinemann, *Chem. Eur. J.* **2004**, *10*, 1899–1905; c) R. W. Saalfrank, C. Deutscher, S. Sperner, T. Nakajima, A. M. Ako, E. Uller, F. Hampel, F. W. Heinemann, *Inorg. Chem.* **2004**, *43*, 4372–4382; d) A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467–469.

[14] a) C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036; b) C. J. Pedersen, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1021–1027.

[15] M. S. Lah, V. L. Pecoraro, *J. Am. Chem. Soc.* **1989**, *111*, 7258–7259.

[16] R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, R. E. P. Winppeny, *J. Chem. Soc., Dalton Trans.* **2000**, 2349–2356.

[17] C. Dendrinou-Samara, C. M. Zaleski, A. Evagorou, J. W. Kampf, V. L. Pecoraro, D. P. Kessissoglou, *Chem. Commun.* **2003**, 2668–2669.

[18] For example, see: G. Psomas, A. J. Stemmler, C. Dendrinou-Samara, J. J. Bodwin, M. Schneider, M. Alexiou, J. W. Kampf, D. P. Kessissoglou, V. L. Pecoraro, *Inorg. Chem.* **2001**, *40*, 1562–1570.

[19] C. Dendrinou-Samara, G. Psomas, L. Iordanidis, V. Tangoulis, D. P. Kessissoglou, *Chem. Eur. J.* **2001**, *7*, 5041–5051.

[20] B. R. Gibney, A. J. Stemmler, S. Pilotek, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1993**, *32*, 6008–6015.

[21] a) D. P. Kessissoglou, J. J. Bodwin, J. W. Kampf, C. Dendrinou-Samara, V. L. Pecoraro, *Inorg. Chim. Acta* **2002**, *331*, 73–80; b) J. A. Halfen, J. J. Bodwin, V. L. Pecoraro, *Inorg. Chem.* **1998**, *37*, 5416–5417; c) B. R. Gibney, H. Wang, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1996**, *35*, 6184–6193; d) A. J. Stemmler, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, *J. Am. Chem. Soc.* **1995**, *117*, 6368–6369; e) B. R. Gibney, D. P. Kessissoglou, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1994**, *33*, 4840–4849.

[22] a) C. Dendrinou-Samara, L. Alevizopoulou, L. Iordanidis, E. Samaras, D. P. Kessissoglou, *J. Inorg. Biochem.* **2002**, *89*, 89–96; b) A. D. Cutland, J. A. Halfen, J. W. Kampf, V. L. Pecoraro, *J. Am. Chem. Soc.* **2001**, *123*, 6211–6212; c) A. J. Stemmler, J. W. Kampf, M. L. Kirk, B. H. Atasi, V. L. Pecoraro, *Inorg. Chem.* **1999**, *38*, 2807–2817; d) A. J. Stemmler, A. Barwinski, M. J. Baldwin, V. Young, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 11 962–11 963; e) A. J. Stemmler, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2841–2843; f) D. P. Kessissoglou, J. W. Kampf, V. L. Pecoraro, *Polyhedron* **1994**, *13*, 1379–1391.

[23] a) M. S. Lah, B. R. Gibney, D. L. Tierney, J. E. Penner-Hahn, V. L. Pecoraro, *J. Am. Chem. Soc.* **1993**, *115*, 5857–5858; b) G. Psomas, C. Dendrinou-Samara, M. Alexiou, A. Tsohos, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **1998**, *37*, 6556–6557.

[24] a) A. J. Stemmler, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1995**, *34*, 2271–2272; b) M. Alexiou, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **2002**, *41*, 4732–4738; c) J.-L. Song, J.-G. Mao, H.-Y. Zeng, R. K. Kremer, Z.-C. Dong, *Inorg. Chem. Commun.* **2003**, *6*, 891–895.

[25] Th. C. Stamatatos, S. Dionyssopoulou, P. Kyritsis, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S. P. Perlepes, *Inorg. Chem.*, in press.

[26] a) M. Alexiou, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, V. Tangoulis, D. P. Kessissoglou, *Eur. J. Inorg. Chem.* **2004**, 3822–3827 ; b) M. Alexiou, C. Dendrinou-Samara, A. Karagianni, S. Biswas, C. M. Zaleski, J. Kampf, D. Yoder, J. E. Penner-Hahn, V. L. Pecoraro, D. P. Kessissoglou, *Inorg. Chem.* **2003**, *42*, 2185–2187; c) M. Alexiou, C. M. Zaleski, C. Dendrinou-Samara, J. Kampf, D. P. Kessissoglou, V. L. Pecoraro, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2348–2355; d) T. Afrati, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, V. Tangoulis, D. P. Kessissoglou, *Angew. Chem. Int. Ed.* **2002**, *41*, 2148–2150.

[27] a) C. J. Milios, P. Kyritsis, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S. P. Perlepes, *Dalton Trans.* **2005**, 501–511; b) C. J. Milios, Th. C. Stamatatos, P. Kyritsis, A. Terzis, C. P. Raptopoulou, R. Vicente, A. Escuer, S. P. Perlepes, *Eur. J. Inorg. Chem.* **2004**, 2885–2901; c) C. J. Milios, E. Kefalloniti, C. P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S. P. Perlepes, *Polyhedron* **2004**, *23*, 83–95; d) C. J. Milios, E. Kefalloniti, C. P. Raptopoulou, A. Terzis, R. Vicente, N. Lalioti, A. Escuer, S. P. Perlepes, *Chem. Commun.* **2003**, 819–821; e) C. J. Milios, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S. P. Perlepes, *Inorg. Chem. Commun.* **2003**, *6*, 1056–1060.

[28] Interesting reviews: a) P. Chaudhuri, *Coord. Chem. Rev.* **2003**, *243*, 143–190; b) V. Yu. Kukushkin, A. J. L. Pombeiro, *Coord. Chem. Rev.* **1999**, *181*, 147–175; c) V. Yu. Kukushkin, D. Tudela, A. J. L. Pombeiro, *Coord. Chem. Rev.* **1996**, *156*, 333–362.

[29] P. Chaudhuri, M. Hess, T. Meyhermüller, E. Bill, H.-J. Haupt, U. Flörke, *Inorg. Chem. Commun.* **1998**, *1*, 39–42.

[30] M. J. Goldcamp, S. E. Robison, J. A. Krause Bauer, M. J. Baldwin, *Inorg. Chem.* **2002**, *41*, 2307–2309.

[31] M. N. Kopylovich, V. Yu. Kukushkin, M. Haukka, J. J. R. Frausto da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 4798–4804.

[32] J. M. Thorpe, R. L. Beddoes, D. Collison, C. D. Garner, M. Helliwell, J. M. Holmes, P. A. Tasker, *Angew. Chem. Int. Ed.* **1999**, *38*, 1119–1121.

[33] J. Lisowski, P. Starynowicz, A. Jezierski, Z. Siatecki, *Polyhedron* **1996**, *15*, 3589–3593.

[34] a) V. V. Pavlishchuk, S. V. Kolotilov, A. W. Addison, M. J. Prushan, D. Schollmeyer, L. K. Thompson, T. Weyhermüller, E. A. Goreshnik, *Dalton Trans.* **2003**, 1587–1595; b) F. Akagi, Y. Michihiro, Y. Nakao, K. Matsumoto, T. Sato, W. Mori, *Inorg. Chim. Acta* **2004**, *357*, 684–688; c) P. Chaaudhuri, M. Hess, E. Rentschler, T. Weyhermüller, U. Flörke, *New J. Chem.* **1998**, *6*, 553–555; d) C. J. Milios, C. P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S. P. Perlepes, A. Escuer, *Angew. Chem. Int. Ed.* **2004**, *43*, 210–212; e) H. Miyasaka, T. Nezu, K. Sugimoto, K. Sugiura, M. Yamashita, R. Clérac, *Inorg. Chem.* **2004**, *43*, 5486–5488.

[35] a) R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12 837–12 844; b) H. Miyasaka, R. Clérac, K. Mizushima, K. Sugiura, M. Yamashita, W. Wernsdorfer, C. Coulon, *Inorg. Chem.* **2003**, *42*, 8203–8213.

[36] a) H.-J. Krüger, G. Peng, R. H. Holm, *Inorg. Chem.* **1991**, *30*, 734–742; b) A. N. Singh, A. Chakravorty, *Inorg. Chem.* **1980**, *19*, 969–971, and references cited therein.

[37] J. A. Cabeza, I. del Rio, V. Rieva, M. Suárez, C. Álvarez-Rúa, S. Garcia-Granda, S. H. Chuang, J. R. Hwu, *Eur. J. Inorg. Chem.* **2003**, 4159–4165.

[38] H. Kumagai, M. Endo, M. Kondo, S. Kawata, S. Kitagawa, *Coord. Chem. Rev.* **2003**, *237*, 197–203.

[39] The full crystallographic formula is $(NH_4)[Zn_5(acac)_2(pko)_6](PF_6)_3 \cdot H_2O \cdot 2.6MeOH$. Crystal data: empirical formula $C_{78.6}H_{78.4}Zn_5N_{19}O_{13}P_3F_{18}$, formula mass 2268.56, crystal size 0.10 × 0.10 × 0.40 mm, monoclinic, $P2/n$, a = 17.903(2), b = 14.875(2), c = 18.745(2) Å, β = 95.33(1)°, V = 4970.2(8) Å^3, Z = 2, $\rho_{calcd.}$ = 1.516 g cm^{-3}, λ(Cu-K_α) = 1.54180 Å, μ = 2.680 mm^{-1}, F(000)= 2298, $2\theta_{max}$ = 103.3°, $-18 \le h \le 0$, $0 \le k \le 15$, $-18 \le l \le 19$.

[40] W. Clegg, D. R. Harbron, C. D. Homan, P. A. Hunt, I. R. Little, B. P. Straughan, *Inorg. Chim. Acta* **1991**, *186*, 51–60.

[41] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C, Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[42] I. Agrell, *Acta Chem. Scand.* **1970**, *24*, 1247–1261.

[43] P. M. Secondo, J. M. Land, R. G. Baughman, H. L. Collier, *Inorg. Chim. Acta* **2000**, *309*, 13–22.

[44] E. O. Schlemper, J. Stunkel, C. Patterson, *Acta Crystallogr., Sect. C* **1990**, *46*, 1226–1228.

[45] a) H.-J. Chen, L.-Z. Zhang, Z.-G. Cai, G. Yang, X.-M. Chen, *J. Chem. Soc., Dalton Trans.* **2000**, 2463–2466; b) H. Adams, N. A. Bailey, D. Fenton, Q.-Y. He, *J. Chem. Soc., Dalton Trans.* **1996**, 2857–2865; c) Y. Ke-Wu, Y. Yuan-Qi, H. Zhong-Xian, W. Yun-Hua, *Polyhedron* **1996**, *15*, 79–81; d) S. R. Petrusenko, V. N. Kokozay, I. O. Fritsky, *Polyhedron* **1997**, *16*, 267–274.

[46] a) A. Erxleben, J. Hermann, *J. Chem. Soc., Dalton Trans.* **2000**, 569–575; b) C. J. Matthews, L. K. Thompson, S. R. Parsons, Z. Xu, D. O. Miller, S. L. Heath, *Inorg. Chem.* **2001**, *40*, 4448–4454.

[47] a) A. K. Boudalis, N. Lalioti, G. A. Spyroulias, C. P. Raptopoulou, A. Terzis, A. Bousseksou, V. Tangoulis, J. P. Tuchagues, S. P. Perlepes, *Inorg. Chem.* **2002**, *41*, 6474–6487; b) I. Chadjistamatis, A. Terzis, C. P. Raptopoulou, S. P. Perlepes, *Inorg. Chem. Commun.* **2003**, *6*, 1365–1371.

[48] G. S. Papaefstathiou, A, Escuer, M. Font-Bardia, S. P. Perlepes, X. Solans, R. Vicente, *Polyhedron* **2002**, *21*, 2027–2032.

[49] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.

[50] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**, pp. 259–263, 282–290.

[51] R. A. Bailey, S. L. Kozak, T. W. Michelsen, W. N. Mills, *Coord. Chem. Rev.* **1971**, *6*, 407–445.

[52] a) G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1986;** b) G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**; c) G. M. Sheldrick, *SHELXL-97, Crystal Structure Refinement Program*, University of Göttingen, Germany, **1997**.

Received: November 4, 2004