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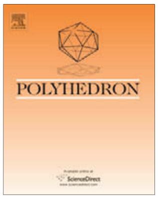

Dinuclear versus trinuclear complex formation in zinc(II) benzoate/pyridyl oxime chemistry depending on the position of the oxime group

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This paper is devoted to Dr. Aris Terzis for his great contribution to the advancement of inorganic chemistry in Greece through single-crystal, X-ray crystallography.

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ABSTRACT

The initial employment of pyridine-3-carbaldehyde oxime, (3-py)C(H)NOH, and pyridine-4-carbaldehyde oxime, (4-py)C(H)NOH, in zinc(II) carboxylate chemistry is reported. The syntheses, crystal structures and IR characterization are described for $[Zn_3(O_2CPh)_6\{(3\text{-py})C(H)NOH\}_2]$ (**1**) and $[Zn_2(O_2CPh)_4\{(4\text{-py})C(H)NOH\}_2]$ (**2**). The trinuclear molecule of **1** has a linear structure, with one monoatomically bridging $\eta^1:\eta^2:\mu$ and two *syn*, *syn*-$\eta^1:\eta^1:\mu$ benzoate groups spanning each pair of Zn^{II} ions; the terminal metal ions are each capped by one (3-py)C(H)NOH ligand coordinating through its pyridyl nitrogen. Complex **2** exhibits a dinuclear paddle–wheel structure with a Zn···Zn distance of 2.990(2) Å; each Zn^{II} ion has a square pyramidal geometry with four carboxylate oxygens in the basal plane and the pyridyl nitrogen of one monodentate (4-py)C(H)NOH ligand at the apex. Both complexes form 1D architectures by virtue of hydrogen bonding interactions involving the free oxime group as donor and the oxime nitrogen (**1**) or carboxylate oxygens (**2**) as acceptors. IR data are discussed in terms of the known structures and coordination modes of the ligands.

1. Introduction

Simple carboxylate anions (RCO_2^-) are ubiquitous and versatile ligands in coordination chemistry. Myriads of complexes with a great variety of metals have been synthesized, many of which have played key roles in the conceptual development of inorganic chemistry [1]. Perhaps most striking in terms of their impact are the so named dinuclear "paddle wheel", the trinuclear "basic" carboxylate and the tetranuclear "butterfly" complexes (Scheme 1). The versatility of the RCO_2^- ligands is reflected in the variety of metal binding modes it can adopt; up to four metal ions have been shown to bind to a single carboxylate ligand. In contrast to the great number of studies concerning $3d^n$, $4d^n$, $5d^n$ (n = 1–9) and 4f-metal carboxylate chemistry, normally associated with other organic coligands, relatively little is known about the group 12 metal carboxylate complexes. One reason for this is the availability of only a limited number of Zn^{II}, Cd^{II} and Hg^{II} carboxylate starting materials in the market.

The current interest in the synthetic, structural and spectroscopic studies of new mononuclear, dinuclear and polynuclear Zn^{II} carboxylate complexes has three main driving forces: (i) the desire to recreate with synthetic models the structure, properties, reactivity and/or function of the mononuclear and dinuclear active sites in Zn^{II} metalloenzymes [2]; (ii) the realization that some Zn^{II} carboxylate complexes based on aromatic ligands are luminescent [3], and; (iii) the fact that some Zn^{II} carboxylates are active catalysts for the coupling of CO_2 and epoxides [4].

There is currently a renewed interest in the coordination chemistry of oximes [5]. The efforts of several research groups are driven by a number of considerations [6]. Pyridyl oximes (Scheme 2) are popular ligands [7] whose anions are versatile ligands for a variety of research objectives. For example, such ligands and especially 2-pyridyl oximes – have been key "players" in the areas of single-molecule [8] and single-chain [9] magnetism. We recently reported [8] the use of methyl 2-pyridyl ketone oxime, (2-py)C(Me)NOH, to prepare $[Mn^{III}_3O(O_2CR)_3\{(2\text{-py})C(Me)NO\}_3]^+$ complexes that were the initial examples of triangular single-molecule magnets, by switching the exchange coupling from the usual antiferromagnetic to ferromagnetic. Moreover, the activation of 2-pyridyl oximes towards further reactivity by 3d-metal centers is also becoming a fruitful area of research [10].

This work describes our initial results in a general programme that can be considered as an amalgamation of the two, above mentioned research areas. The project concerns the study of the reactions of Zn^{II} *carboxylate* sources and *simple* pyridyl oximes

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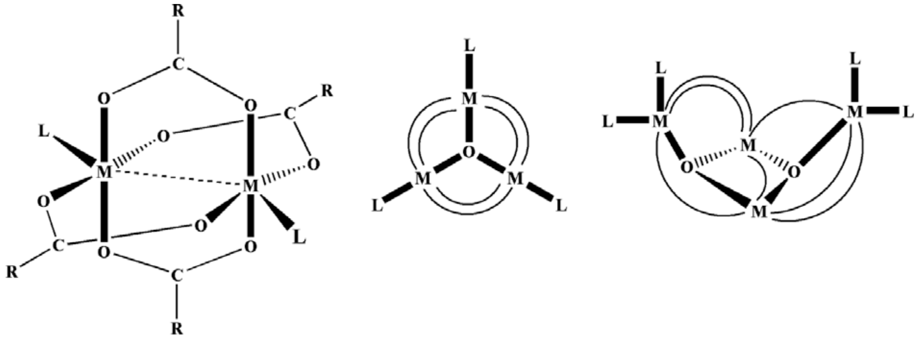
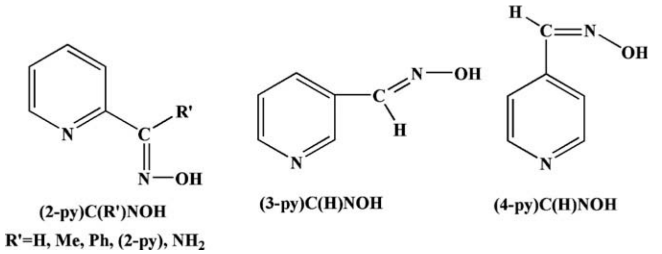


Scheme 1. Paddle wheel (left), trinuclear basis carboxylate (middle) and tetranuclear "butterfly" carboxylate (right) complexes. Curved lines represent bidentate bridging carboxylate groups. The paddle wheel structural type is associated with a variety of metal–metal interactions ranging from no interaction, weak spin-pairing, various orders of metal–metal bonding, to the "super-short" metal–metal bonds. The L groups are often monodentate ligands, but they may represent intercluster association into polymeric structures or (only in the case of the "butterfly" complexes) one donor atom of a bidentate chelate.



Scheme 2. General structural formula and abbreviation of the 2-pyridyl oximes that are used in our laboratories (left); the ligands pyridine-3-carbaldehyde oxime [3-pyridinealdoxime, (3-py)C(H)NOH] and pyridine-4-carbaldehyde oxime [4-pyridinealdoxime, (4-py)C(H)NOH] employed in this work are shown in the middle and right part, respectively, of the scheme.

(the term "simple" means here ligands with only one pyridyl and one oxime group as donors). Our goals are to investigate if clusters and coordination polymers can be prepared from the Zn^{II}/RCO_2^-/(py)C(R′)NOH reaction systems (R′=H, Me, Ph) and to isolate, if possible, photoluminescent complexes. Reactions of $Zn(O_2CR)_2{\cdot}2H_2O$ (R = Me, Ph) with the more complex ligand di-2-pyridyl ketone oxime, (2-py)C(2-py)NOH, have led to compounds $[Zn_4(OH)_2(O_2CR)_2\{(2\text{-py})C(2\text{-py})NO\}_4]$ [11] with the extremely rare inverse 12-metallacrown-4 structural motif. We report here the preparation and characterization of two complexes derived from the reactions of $Zn(O_2CPh)_2{\cdot}2H_2O$ with (3-py)C(H)NOH and (4-py)C(H)NOH (see Scheme 2). Efforts to date with the isomeric pyridine-*x*-carbaldehyde oximes [*x* = 2, (2-py)C(H)NOH, R′ = H in Scheme 2; *x* = 3, (3-py)C(H)NOH; *x* = 4, (4-py)C(H)NOH] have almost completely neglected Zn chemistry; no Zn^{II} complexes of (3-py)C(H)NOH and (4-py)C(H)NOH have been reported, while the only structurally characterized Zn^{II}/(2-py)C(H)NOH or (2-py)C(H)NO⁻ compound is $[Zn_4(OH)_2Cl_2\{(2\text{-py})C(H)NO\}_4]$ [12].

2. Experimental

2.1. General and spectroscopic measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. $Zn(O_2CPh)_2{\cdot}2H_2O$ was prepared by the reaction of $Zn(O_2CMe)_2{\cdot}2H_2O$ with and excess of $PhCO_2H$ in $CHCl_3$ under reflux. Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer.

IR spectra (4000–450 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT-spectrometer with samples prepared as KBr pellets.

2.2. Compound preparation

2.2.1. $[Zn_3(O_2CPh)_6\{(3\text{-py})C(H)NOH\}_2]$ (**1**)

A solution of $Zn(O_2CPh)_2{\cdot}2H_2O$ (0.346 g, 1.00 mmol) in MeCN (10 ml) was added gradually to a stirred solution of (3-py)C(H)NOH (0.122 g, 1.00 mmol) in MeCN (10 ml). Slow evaporation of the resulting solution at room temperature yielded colourless prismatic crystals of **1** after three days. The crystals were collected by filtration under vacuum, washed with MeCN (2 × 5 ml) and Et_2O (5 ml), and dried in air. Typical yields were in the 50–55% range (based on the metal). FT-IR (KBr pellet, cm^{-1}): 3354mb, 3064w, 1622sh, 1612vs, 1602m, 1570s, 1540m, 1490m, 1448w, 1400vs, 1304m, 1192w, 1130w, 1058w, 1026w, 978m, 890w, 874w, 838w, 814w, 720s, 700m, 670m, 654w, 586w, 528w, 446w. *Anal.* Calc. for $C_{54}H_{42}N_4O_{14}Zn_3$ (1167.03): C, 55.57; H, 3.63; N, 4.80. Found: C, 55.29; H, 3.37; N, 4.82%.

2.2.2. $[Zn_2(O_2CPh)_4\{(4\text{-py})C(H)NOH\}_2]$ (**2**)

To a stirred solution of $Zn(O_2CPh)_2{\cdot}2H_2O$ (0.138 g, 0.40 mmol) in MeCN (10 ml) was added a solution of (4-py)C(H)NOH (0.049 g, 0.40 mmol) in the same solvent (10 ml). The reaction solution was stirred for 15 min during which time a white solid precipitated. The precipitate was collected by filtration and the filtrate was allowed to slowly evaporate at room temperature. After

Table 1
Crystallographic data for complexes **1** and **2**.

Parameter	1	2
Chemical formula	$C_{54}H_{42}N_4O_{14}Zn_3$	$C_{40}H_{32}N_4O_{10}Zn_2$
Formula weight	1167.09	859.48
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	10.414(4)	16.485(8)
b (Å)	10.830(4)	13.008(6)
c (Å)	12.690(5)	19.982(9)
α (°)	81.66(1)	90
β (°)	79.73(1)	113.31(2)
γ (°)	66.40(1)	90
V (Å³)	1286.2(9)	3935(3)
Z	1	4
T (K)	298	298
Radiation, wavelength Mo Kα	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.507	1.451
μ (mm^{-1})	1.459	1.281
Data collected/unique (R_{int})	4800/4529 (0.014)	6082/5893 (0.031)
Data with $I > 2\sigma(I)$	3719	3735
R_1[a] [$I > 2\sigma > (I)$]	0.0361	0.0516
wR_2[b] [unique data]	0.1159	0.1203

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

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

three days, X-ray quality colourless crystals of **2** were collected by filtration under vacuum, washed with MeCN (2 × 5 ml) and Et_2O (5 ml), and dried in air. Typical yields (including the white solid) were in the 50–55% range. FT-IR (KBr pellet, cm^{-1}): 3221mb, 3066w, 1634vs, 1573s, 1409vs, 1301m, 1225w, 1175vw, 1067vw, 1030w, 990m, 932w, 832m, 714s, 673m, 560w, 536m, 472w, 460w. The IR spectra of the white powder and the colourless crystals (in the form of a powder) are identical. *Anal.* Calc. for $C_{40}H_{32}N_4O_{10}Zn_2$ (859.44): C, 55.90; H, 3.76; N, 6.52. Found: C, 55.62; H, 3.78; N, 6.55%.

2.3. Single-crystal X-ray crystallography

A colourless crystal of **1** (0.10 × 0.20 × 0.60 mm) and a colourless crystal of **2** (0.20 × 0.30 × 0.50 mm) were mounted in air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo Kα radiation. Details for data collection and processing are listed in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23°$. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using Crystal Logic software. Ψ-scan data were collected for both structures. The intensity of a certain reflection remains invariant during 360° rotation around the Φ axis, thus absorption correction is not required.

The structures were solved by direct methods using SHELXS-86 [13] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [14]. Further experimental crystallographic details for **1**: $2\theta_{max} = 50°$; 424 parameters refined; $(\Delta/\sigma)_{max} = 0.000$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0.557/-0.712$ e/Å^3; R_1 (for all data), 0.0581. All hydrogen atoms were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically. Further experimental crystallographic details for **2**: $2\theta_{max} = 47.2°$; 633 parameters refined; $(\Delta/\sigma)_{max} = 0.002$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0.292/-0.354$ e/Å^3; R_1 (for all data), 0.1075. All hydrogen atoms were located by difference maps and were refined isotropically. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Brief synthetic comments and IR spectra

The chemical and structural identities of the products from the $Zn(O_2CPh)_2{\cdot}2H_2O$/LH reaction systems in MeCN, where LH is (3-py)C(H)NOH or (4-py)C(H)NOH, depends on the pyridyl oxime ligand. Use of (3-py)C(H)NOH gives the trinuclear cluster **1**, whereas employment of (4-py)C(H)NOH led to the dinuclear compound **2**.

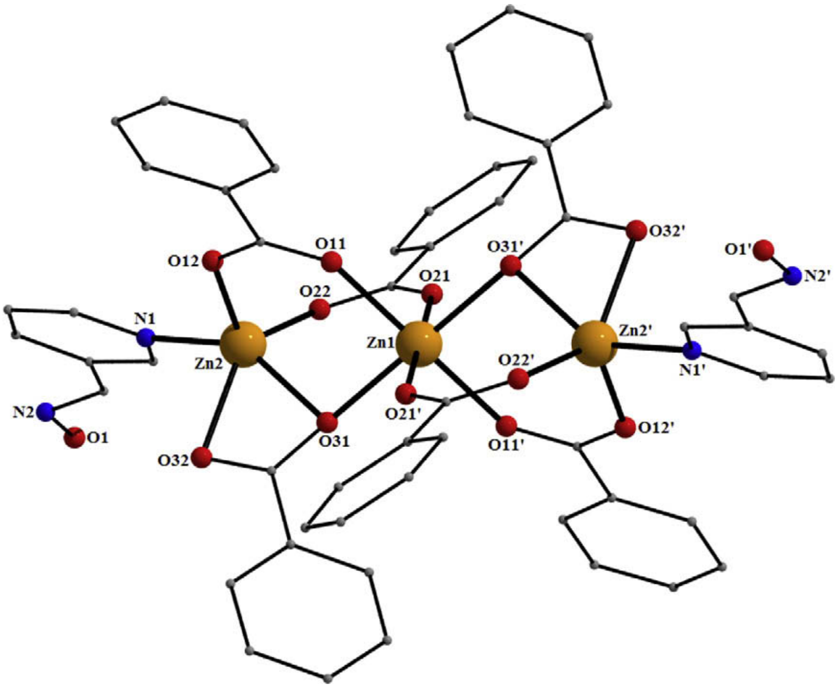


Fig. 1. Partially labeled plot of the molecular structure of **1**. H atoms have been omitted for clarity. Colour code: Zn, orange; O, red; N, blue; C, gray. Primes are used for symmetry related ($-x$, $1-y$, $-z$) atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

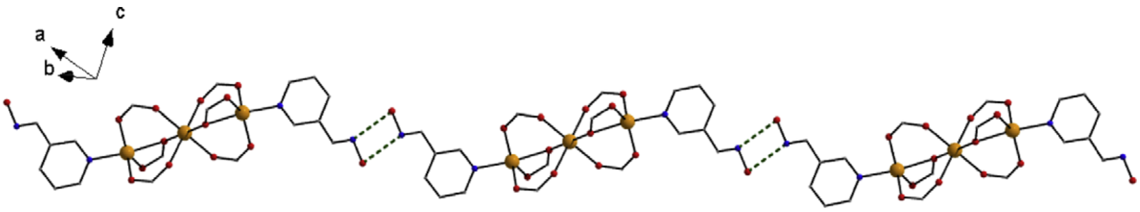


Fig. 2. A part of the 1D structure of **1** due to H-bonding interactions (green dashed lines); colour code as in Fig. 1. H atoms and the phenyl rings of the benzoates have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

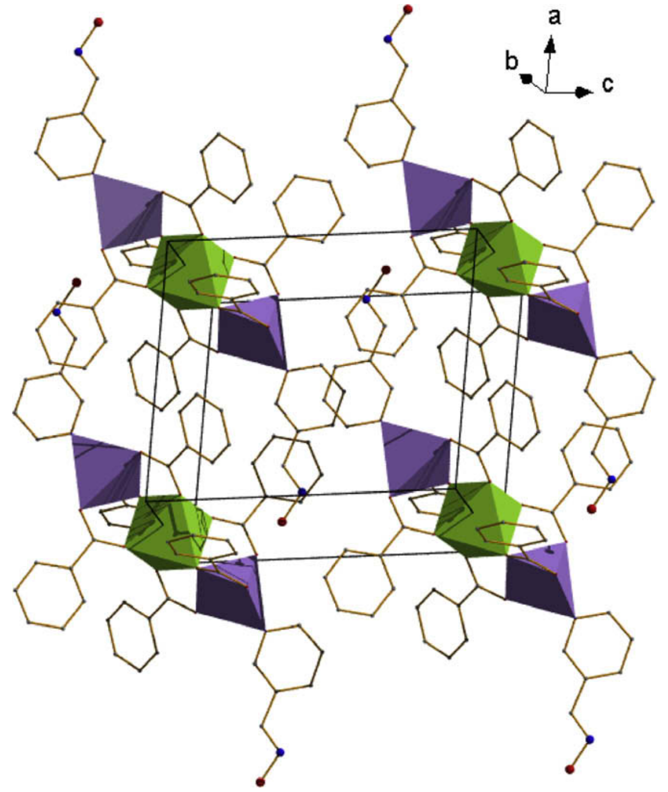


Fig. 3. Crystal packing diagram of complex **1**. The metal coordination spheres are represented as polyhedra [Zn(1), green; Zn(2), purple]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The preparation of the two complexes is summarized in the balanced Eqs. (1) and (2):

$$3\mathrm{Zn(O_2CPh)_2}\cdot 2\mathrm{H_2O} + 2\mathrm{(3\text{-}py)C(H)NOH} \xrightarrow{\mathrm{MeCN}} [\mathrm{Zn_3(O_2CPh)_6\{(3\text{-}py)C(H)NOH\}_2}] + 6\mathrm{H_2O} \qquad (1)$$

$$2\mathrm{Zn(O_2CPh)_2}\cdot 2\mathrm{H_2O} + 2\mathrm{(4\text{-}py)C(H)NOH} \xrightarrow{\mathrm{MeCN}} [\mathrm{Zn_2(O_2CPh)_4\{(4\text{-}py)C(H)NOH\}_2}] + 4\mathrm{H_2O} \qquad (2)$$

Two features of the reactions represented by the chemical (1) and (2) deserve comments. First, the "wrong" reaction ratio (1:1) employed for the preparation of **1**, compared to the stoichiometric ratio (1.5:1) required by Eq. (1), obviously did not prove detrimental to the formation of the complex. With the identity of **1** crystallographically established (vide infra), the "correct" stoichiometric ratio, i.e. $\mathrm{Zn^{II}}$:(3-py)C(H)NOH = 1.5:1, was employed and led to the pure compound in very good yield (60–65%). Second, complexes **1** and **2** seem to be the only isolable products from the $\mathrm{Zn(O_2CPh)_2{\cdot}2H_2O}$/LH reaction systems. The $\mathrm{Zn^{II}}$ to ligand reaction ratio (we used 1:2 and 1:3 ratios to "force" the formation of mononuclear complexes, e.g. $[\mathrm{Zn(O_2CPh)_2(LH)}_x]$ with $x = 2$ or 3), the presence of counteranions (we added $\mathrm{ClO_4}^-$ or $\mathrm{PF_6}^-$ in some reaction mixtures to "force" the isolation of cationic complexes), the nature of the solvent (use of alcohols gives the same products) and the precipitation/crystallization method have no influence on the identity of the products.

The IR spectra of **1** and **2** exhibit medium intensity bands at ~3350 and 3320 $\mathrm{cm^{-1}}$, respectively, assignable to the ν(OH) vibration of the coordinated pyridyl oxime ligands [6a,15]. The broadness and low frequency of these bands are both indicative of hydrogen bonding. The medium intensity bands at 1636 and 1124 $\mathrm{cm^{-1}}$ in the spectrum of the free ligand (3-py)C(H)NOH are assigned to $\nu(\mathrm{C{=}N})_{\mathrm{oxime}}$ and $\nu(\mathrm{N{-}O})_{\mathrm{oxime}}$, respectively [6a,16]. The corresponding vibrations in the spectrum of free (4-py)C(H)-NOH appear at 1566 and 1096 $\mathrm{cm^{-1}}$. In the spectra of the complexes, these typical bands of the neutral oxime group are situated at approximately the same wavenumbers to those in the spectra of the corresponding free ligands, confirming the crystallographically established (vide infra) non-participation of the oxime group in coordination. For example, the $\nu(\mathrm{C{=}N})_{\mathrm{oxime}}$ and $\nu(\mathrm{N{-}O})_{\mathrm{oxime}}$ vibrations appear at 1622 and 1130 $\mathrm{cm^{-1}}$, respectively, in the spectrum of **1**. The in-plane deformation band of the pyridyl ring of the free ligands [638 $\mathrm{cm^{-1}}$ in (3-py)C(H)NOH, 646 $\mathrm{cm^{-1}}$ in (4-py)C(H)NOH] shifts upwards in the complexes (654 $\mathrm{cm^{-1}}$ in **1**, 673 $\mathrm{cm^{-1}}$ in **2**), confirming the involvement of the ring-N atom in coordination [17]. The strong bands at 1573 and 1409 $\mathrm{cm^{-1}}$ in

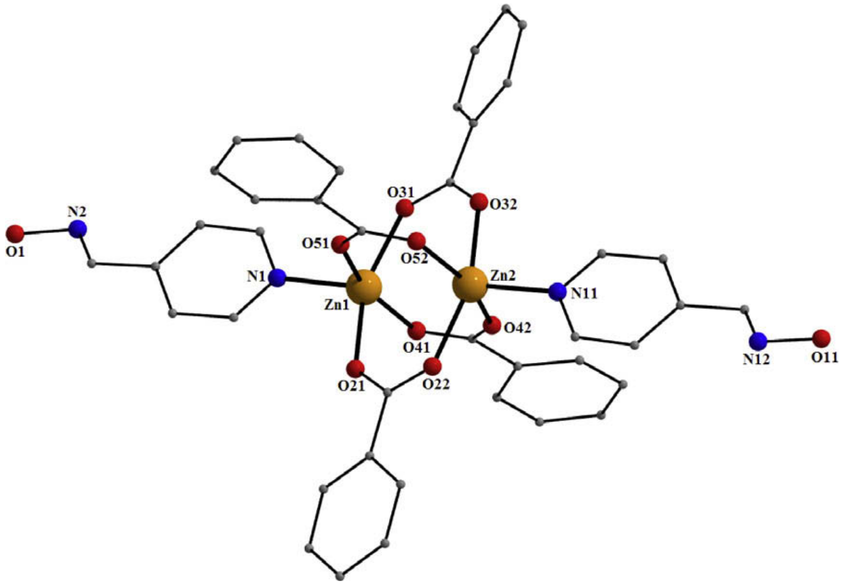


Fig. 4. Partially labeled plot of the molecular structure of **2**. Colour code as in Fig. 1. H atoms have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

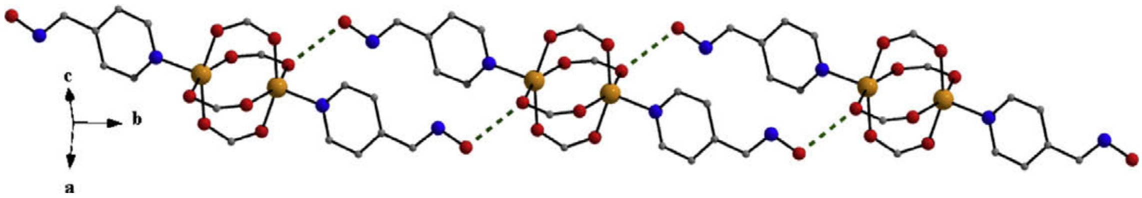


Fig. 5. A small portion of the ladder-like 1D architectures of **2** due to H-bonding interactions (green dashed lines). Colour code as in Fig. 1. The H atoms and the phenyl rings of the benzoates have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

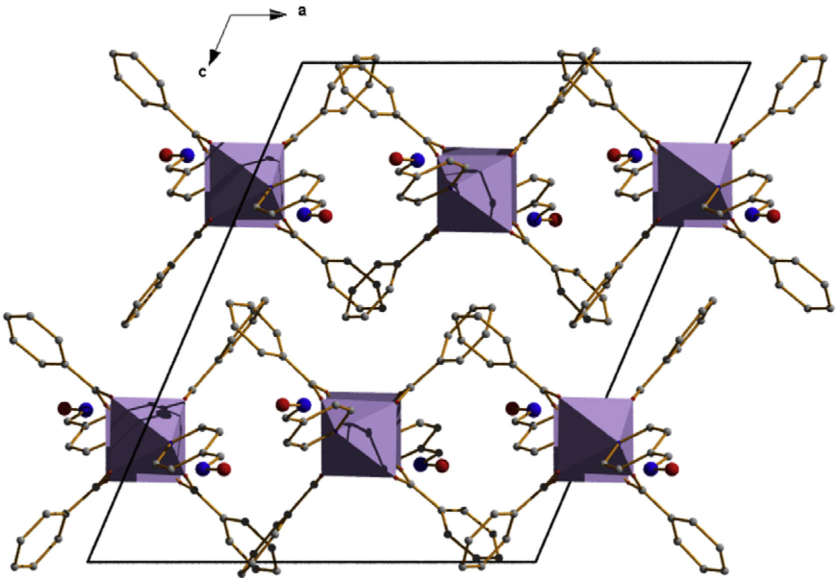


Fig. 6. Crystal packing diagram of complex **2**. The metal coordination spheres are represented as polyhedra (purple colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Selected interatomic distances (Å) and angles (°) for complex **1**.

Distances			
Zn(1)–O(11)	2.084(3)	Zn(2)–O(12)	1.955(3)
Zn(1)–O(21)	2.069(3)	Zn(2)–O(22)	1.951(3)
Zn(1)–O(31)	2.144(3)	Zn(2)–O(31)	2.147(3)
Zn(1)–O(11′)	2.084(3)	Zn(2)–O(32)	2.202(3)
Zn(1)–O(21′)	2.069(3)	Zn(2)–N(1)	2.073(4)
Zn(1)–O(31′)	2.144(3)	Zn(1)···Zn(2)	3.392(5)
Angles			
O(11)–Zn(1)–O(21)	93.6(1)	O(11′)–Zn(1)–O(31′)	90.2(1)
O(11)–Zn(1)–O(31)	90.2(1)	O(21′)–Zn(1)–O(31′)	90.3(1)
O(11)–Zn(1)–O(11′)	180.0	O(12)–Zn(2)–O(22)	113.9(1)
O(11)–Zn(1)–O(21′)	86.4(1)	O(12)–Zn(2)–O(31)	107.9(1)
O(11)–Zn(1)–O(31′)	89.8(1)	O(12)–Zn(2)–O(32)	105.7(1)
O(21)–Zn(1)–O(31)	90.3 (1)	O(12)–Zn(2)–N(1)	99.5(1)
O(11′)–Zn(1)–O(21)	86.4(1)	O(22)–Zn(2)–O(31)	94.4(1)
O(21)–Zn(1)–O(21′)	180.0	O(22)–Zn(2)–N(1)	93.2(2)
O(21)–Zn(1)–O(31′)	89.7(1)	O(31)–Zn(2)–N(1)	145.5(1)
O(11′)–Zn(1)–O(31)	89.8(1)	O(22)–Zn(2)–O(32)	138.1(1)
O(21′)–Zn(1)–O(31)	89.7(1)	O(31)–Zn(2)–O(32)	59.9(1)
O(31)–Zn(1)–O(31′)	180.0	O(32)–Zn(2)–N(1)	93.1(1)
O(11′)–Zn(1)–O(21′)	93.6(1)		

Symmetry operations used to generate equivalent atoms: (′) −*x*, 1 − *y*, −*z*.

the spectrum of **2** are assigned to the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes of the benzoato ligands, respectively [18]; the former may also involve a pyridyl stretching character. The difference Δ, where $\Delta = \nu_{as}(CO_2) - \nu_s(CO_2)$, is 164 cm^{-1}, less than that for NaO_2CPh (184 cm^{-1}), as expected for bidentate bridging ligation [18]. In the IR spectrum of **1**, the bands at 1570 and 1612 cm^{-1} are assigned to $\nu_{as}(CO_2)$; both may also involve a pyridyl stretching character. The $\nu_s(CO_2)$ modes appear at 1400 and 1448 cm^{-1}. The appearance of two distinct bands for each mode reflects the presence of two different types of $PhCOO^-$ groups in the complex (vide infra) [19]. The 1612, 1400 cm^{-1} pair ($\Delta = 212$ cm^{-1}) are assigned [18–20] to the $\eta^1:\eta^2:\mu_2$ benzoate, while the 1570, 1448 cm^{-1} pair ($\Delta = 122$ cm^{-1}) to the bidentate bridging ($\eta^1:\eta^1:\mu_2$) benzoates.

3.2. Description of structures

Aspects of the molecular and crystal structures of complexes **1** and **2** are shown in Figs. 1–6. Selected interatomic distances and angles are listed in Tables 2 and 4, while important hydrogen bonding interactions are presented in Table 5.

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. Its crystal structure consists of trinuclear $[Zn_3(O_2CPh)_6\{(3\text{-py})C(H)NOH\}_2]$ molecules. The central metal center [Zn(1)] is located on a crystallographic inversion center and thus the trinuclear molecule adopts a strictly linear structure. Zn(1) is coordinated by six oxygen atoms belonging to six $PhCO_2^-$ groups. One $\eta^1:\eta^2:\mu$ and two *syn*, *syn*-$\eta^1:\eta^1:\mu$ carboxylate groups span each pair of neighbouring Zn^{II} ions. The terminal metal ions [Zn(2), Zn(2′)] are each capped by one monodentate (3-py)C(H)NOH ligand; the donor atom of (3-py)C(H)NOH is the pyridyl nitrogen. The ZnO_6 octahedron is almost perfect with the Zn(1)–O bond lengths and the cis O–Zn(1)–O bond angles being in the ranges 2.069(3)–2.144(3) Å and 86.4(1)–93.6(1)°, respectively. The coordination geometry about the terminal Zn^{II} ions is described as distorted square pyramidal with the carboxylate oxygen atoms O(12) and O(12′) occupying the apical positions for Zn(2) and Zn(2′), respectively. Analysis of the shape-

Table 3
Pentinent structural properties[a] for trinuclear Zn^{II} complexes containing the $[Zn^{II}_3(\eta^1{:}\eta^1{:}\mu\text{-}O_2CPh)_4(\eta^1{:}\eta^2{:}\mu\text{-}O_2CPh)_2]$ unit.

Complex	*B* (Å)	*D* (Å)	*A* (Å)	Zn···Zn (Å)	C–O$_b$ (Å)	C–O$_d$ (Å)	*θ* (°)	*β* (°)	*α* (°)
$[Zn_3(O_2CPh)_6(py)_2]$[b,c]	2.328	2.121	2.141	3.444	1.248	1.241	100.73	86.43	139.45
$[Zn_3(O_2CPh)_6\ (2,3\text{-}Me_2pyz)_2]$[d]	2.103	2.264	2.207	3.370	1.278	1.242	102.85	94.03	139.05
Complex **1**[e]	2.147	2.202	2.144	3.392	1.271	1.247	101.46	91.38	145.52

Abbreviations: 2,3-Me_2pyz = 2,3-dimethylpyrazine; py = pyridine.
[a] See Scheme 3 for the definition of the various structural parameters given in this table.
[b] Ref. [22b].
[c] This discrete cluster cocrystallizes with $[Zn_2(O_2CPh)_4(py)_2]$ in the complex.
[d] Ref. [22b].
[e] This work.

Table 4
Selected interatomic distances (Å) and angles (°) for complex **2**.

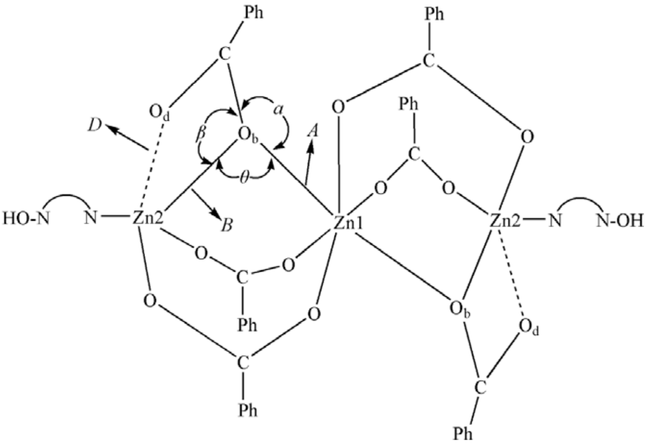
Distances			
Zn(1)–O(31)	2.007(5)	Zn(2)–O(32)	2.019(5)
Zn(1)–O(21)	2.014(5)	Zn(2)–N(11)	2.028(4)
Zn(1)–N(1)	2.028(4)	Zn(2)–O(52)	2.070(4)
Zn(1)–O(41)	2.061(4)	Zn(2)–O(42)	2.105(5)
Zn(1)–O(51)	2.132(5)	Zn(2)–O(22)	2.017(5)
Zn(1)···Zn(2)	2.990(2)		
Angles			
O(31)–Zn(1)–O(21)	157.2(2)	O(22)–Zn(2)–O(32)	158.8(2)
O(21)–Zn(1)–N(1)	100.5(2)	O(32)–Zn(2)–N(11)	98.8(2)
O(21)–Zn(1)–O(41)	89.4(2)	O(32)–Zn(2)–O(52)	89.0(2)
O(31)–Zn(1)–O(51)	89.6(2)	O(22)–Zn(2)–O(42)	88.1(2)
N(1)–Zn(1)–O(51)	93.4(2)	N(11)–Zn(2)–O(42)	94.7(2)
O(31)Zn(1)N(1)	102.2(2)	O(22)–Zn(2)–N(11)	102.0(2)
O(31)Zn(1)O(41)	86.5(2)	O(22)–Zn(2)–O(52)	88.6(2)
N(1)–Zn(1)–O(41)	107.2(2)	N(11)–Zn(2)–O(52)	107.6(2)
O(21)–Zn(1)–O(51)	86.5(2)	O(32)–Zn(2)–O(42)	86.2(2)
O(41)–Zn(1)–O(51)	159.5(2)	O(52)–Zn(2)–O(42)	157.7(2)

determining angles using the approach of Reedijk and co-workers [21] yields a trigonality index, τ, value of 0.12 (τ = 0 and 1 for perfect *sp* and *tbp* geometries, respectively). The coordination of the bridging benzoate oxygen [O(31), O(31′)] is slightly pyramidal [$\sum$O(31) = 341.4(1)°]. The Zn(1)–O(31)–Zn(2) angle is 104.5(1)°.

In the crystal lattice of **1**, the molecules interact through hydrogen bonds building 1D chains parallel to the [2 0 −1] vector.

Complex **1** is the third structurally characterized Zn^{II}_3 complex containing the $[Zn^{II}_3(\eta^1{:}\eta^1{:}\mu_2\text{-}O_2CPh)_4(\eta^1{:}\eta^2{:}\mu_2\text{-}O_2CPh)_2]^0$ unit. The other two complexes are $[Zn_3(O_2CPh)_6(2,3\text{-}Me_2pyz)_2]$ [22a] and the trinuclear part of complex $[Zn_3(O_2CPh)_6(py)_2]\cdot[Zn_2(O_2CPh)_4(py)_2]$ [22b], where 2,3-Me_2pyz and py are 2,3-dimethylpyrazine and pyridine, respectively. Such complexes have been important in the establishment of the "carboxylate shift" concept [23]. Of the various types of metal-carboxylate binding modes, monoatomic bridging between metal ions offers great flexibility. Analysis [23] of the structural characteristics of dinuclear and trinuclear complexes containing monoatomically bridging carboxylate groups reveals that they can be grouped into three classes, depending upon the strength of the interaction of the non-bridging, or dangling (O_d), oxygen atom [O(32) in compound **1**] with one of the bridged metal centers [Zn(2) in **1**]. The application of this analysis to trinuclear Zn^{II} benzoate complexes is demonstrated in Scheme 3 and Table 3. The monoatomic bridging mode is postulated to be an important intermediate between the other, more common carboxylate binding modes, based on observed variation of the geometry for monoatomic bridges in structurally characterized metal complexes. The "movement" from monoatomic bridging to the other binding modes has been termed "carboxylate shift" [23]; such a shift is considered to be kinetically important in carboxylate-containing metalloproteins. Complex **1** is characterized by a moderate *D* value, *D* > *B*, *A*, a rather long Zn···Zn distance, a difference between C–O_d and C–O_b and a distinct tilt (α–β) of the $\eta^1{:}\eta^2{:}\mu$ carboxylate group towards Zn(2); thus, this compound can be placed in class II in Lippard's "carboxylate shift" classification scheme [23].

Compound **1** joins only a handful of structurally characterized metal complexes of (3-py)C(H)NOH [24]; in all the previously reported complexes the 3-pyridinealdoxime ligand is attached to the metal ions through the pyridine nitrogen atom (like in **1**) with



Scheme 3. Schematic structure of complex **1** showing the dangling (O_d) and bridging (O_b) oxygen atoms of the $\eta^1{:}\eta^2{:}\mu_2$ carboxylate groups, and defining the geometry of monoatomic carboxylate-bridged polymetallic centers in relation to the "carboxylate shift" mechanism proposed by Lippard and co-workers [23]; the values of the relevant structural parameters for **1** and the other two, structurally characterized complexes containing the $[Zn^{II}_3(\eta^1{:}\eta^1{:}\mu\text{-}O_2CPh)_4(\eta^1{:}\eta^2{:}\mu\text{-}O_2CPh)_2]^0$ unit are listed in Table 3.

Table 5
Hydrogen bonding interactions in **1** and **2**.

Interaction D–H···A	D···A (Å)	H···A (Å)	D–H···A (°)	Symmetry operation of A
1				
O1–HO1···N2	2.894(6)	1.94(8)	159(7)	2 − *x*, 1 − *y*, −1 − *z*
2				
O1–HO1···O52	2.727(7)	1.92(8)	169(8)	*x*, −1 + *y*, *z*
O11–HO11···O41	2.781(7)	2.05(11)	157(11)	*x*, 1 + *y*, *z*

the free oxime group participating in hydrogen bonding interactions. Complex **1** is the first Zn^{II} complex of (3-py)C(H)NOH.

Complex **2** crystallizes in the monoclinic space group $P2_1/n$. The four *syn*, *syn*-η^1:η^1:μ $PhCO_2^-$ ligands display a paddle wheel arrangement about the Zn···Zn axis. Each Zn^{II} center has a square pyramidal coordination geometry [$\tau = 0.04$ for Zn(1) and 0.02 for Zn(2)], with the apex provided by coordination of the pyridyl nitrogen atom of a monodentate (4-py)C(H)NOH ligand. The metal to apical atom distances are the same, i.e., 2.028(4) Å. The mean Zn–O(carboxylate) bond lengths are 2.054(5) Å for Zn(1) and 2.053(5) Å for Zn(2). These distances are typical and unremarkable [25]. Zn(1) lies 0.386 Å and Zn(2) lies 0.387 Å out of their respective least-squares basal planes towards N(1) and N(11), respectively. The Zn(1)···Zn(2)–N(11) and Zn(2)···Zn(1)–N(1) angles are the same, i.e. 160.8°. Dinuclear $[Zn_2(O_2CR)_4L_2]$ complexes (L = monodentate ligand) have previously been observed to be either collinear [26] or similarly offset [25]. The tetracarboxylate bridging framework can accommodate metal–metal separations of up to ~3.5 Å [25]. The Zn···Zn separation in **1** [2.990(2) Å] is shorter than this maximum, but longer than the Cu···Cu distances in structurally similar Cu_2^{II} complexes [27].

In the crystal lattice of **2**, the dinuclear molecules interact through hydrogen bonds forming double, ladder-like chains along the *b* axis (Table 5, Fig. 5). Both oxime groups act as donors to carboxylate oxygen atoms.

Complex **2** is a new member of a small family of paddle wheel $[Zn_2(O_2CPh)_4L_2]$ complexes [22,28]. It is the sixth structurally characterized metal complex of (4-py)C(H)NOH. The previously reported complexes $[UO_2(acac)_2\{(4\text{-py})C(H)NOH\}]$ [29a], $[Cu(ClO_4)_2(phen)\{(4\text{-py})C(H)NOH\}_2]\cdot(4\text{-py})C(H)NOH$ [29b], $[Ni\{(4\text{-py})C(H)NOH\}_4(H_2O)_2]Br_2\cdot 2(4\text{-py})C(H)NOH$ [29c], $[Ag_4Mn_2(CN)_8\{(4\text{-py})C(H)NOH\}_4(H_2O)_2]_n$ [29d] and $[Cu(dipic)\{(4\text{-py})C(H)NOH\}(H_2O)]$ [29e], where $acac^-$ is the pentane-2,4-dionato (−1) ion and $dipic^{2-}$ is the pyridine-2,6-dicarboxylato (−2) ligand, all involve monodentate (4-py)C(H)NOH ligands with the pyridine nitrogen as the donor atom.

4. Concluding comments and perspectives

The initial use of (3-py)C(H)NOH and (4-py)C(H)NOH in reactions with $Zn(O_2CPh)_2\cdot 2H_2O$ has yielded the first Zn^{II} complexes of these ligands; the complexes have interesting molecular and crystal structures. The nuclearity of the product depends on the isomeric ligand form used. This work demonstrates the synthetic potential of combining 3- or 4-pyridinealdoxime with carboxylate ligands. Complexes **1** and **2** augur well that they are merely the first members of a new family of 3d-metal carboxylate clusters with (*x*-py)C(H)NOH-based ligands (*x* = 2, 3, 4). We currently investigate several M^{II}/RCO_2^-/(3-py)C(H)NOH or (4-py)C(H)NOH reaction systems ($M^{II} = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}$; R = Me, CMe_3, Ph) as an entry point to clusters with various nuclearities and structural types.

Metal complexes with *N*, *O*- or *N*,*N*′-bidentate bridging behaviours of the two ligands or complexes in which the oxime functionality is deprotonated are not known to date, and it is currently not evident if such species could be capable of existence; such complexes could be high nuclearity clusters or coordination polymers. We are studying these matters. It is also clear that the M^{II}/(3-py)C(H)NOH or (4-py)C(H)NOH chemistry warrants expansion to anionic ligands other than carboxylates, e.g. NO_3^-, SO_4^{2-}, etc.

5. Supplementary data

CCDC 727528 and 727529 contains the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] (a) R.C. Mehrotra, R. Bohra, Metal Carboxylates, Academic Press, New York, 1983;
(b) J. Catterick, P. Thornton, Adv. Inorg. Chem. Radiochem. 20 (1977) 291;
(c) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem. Int. Ed. 43 (2004) 1466.
[2] (a) W.N. Lipscomb, W. Sträter, Chem. Rev. 96 (1996) 2375;
(b) R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239.
[3] M.-L. Tong, S.-L. Zheng, J.-X. Shi, Y.-X. Tong, H.K. Lee, X.-M. Chen, J. Chem. Soc., Dalton Trans. (2002) 1727.
[4] (a) D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, Inorg. Chem. 41 (2002) 973;
(b) D.J. Darensbourg, M.S. Zimmer, Macromolecules 32 (1999) 2137.
[5] (a) V.Yu. Kukushkin, A.J.L. Pombeiro, Coord. Chem. Rev. 181 (1999) 147;
(b) A.G. Smith, P.A. Tasker, D.J. White, Coord. Chem. Rev. 241 (2003) 61.
[6] (a) C. Papatriantafyllopoulou, C.G. Efthymiou, C.P. Raptopoulou, A. Terzis, E. Manessi-Zoupa, S.P. Perlepes, Spectrochim. Acta, Part A 70 (2008) 718. and references therein;
(b) C.J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S.P. Perlepes, G. Christou, E.K. Brechin, J. Am. Chem. Soc. 129 (2007) 12505.
[7] (a) P. Chaudhuri, Coord. Chem. Rev. 243 (2003) 143;
(b) C.J. Milios, Th.C. Stamatatos, S.P. Perlepes, Polyhedron 25 (2006) 134. Polyhedron Report.
[8] Th.C. Stamatatos, D. Foguet-Albiol, S.-C. Lee, C.C. Stoumpos, C.P. Raptopoulou, A. Terzis, W. Wernsdorfer, S.O. Hill, S.P. Perlepes, G. Christou, J. Am. Chem. Soc. 129 (2007) 9484.
[9] H. Miyasaka, R. Clèrac, K. Mizushima, K. Sugiura, M. Yamasita, W. Wernsdorfer, C. Coulon, Inorg. Chem. 42 (2003) 8203.
[10] (a) H. Kumagai, M. Endo, M. Kondo, S. Kawata, S. Kawata, S. Kitagawa, Coord. Chem. Rev. 237 (2003) 197;
(b) C.J. Milios, P. Kyritsis, C.P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer, S.P. Perlepes, Dalton. Trans. (2005) 501;
(c) C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, A. Escuer, R. Vicente, S.P. Perlepes, Polyhedron 23 (2004) 83.
[11] (a) M. Alexiou, E. Katsoulakou, C. Dendrinou-Samara, C.P. Raptopoulou, V. Psycharis, E. Manessi-Zoupa, S.P. Perlepes, D.P. Kessissoglou, Eur. J. Inorg. Chem. (2005) 1964;
(b) A.J. Stemmler, J.W. Kampf, V.L. Pecoraro, Inorg. Chem. 34 (1995) 2271.
[12] J.-L. Song, J.-G. Mao, H.-Y. Zeng, R.K. Kremer, Z.-C. Dong, Inorg. Chem. Commun. 6 (2003) 891.
[13] G.M. Sheldrick, SHELXS-86, Structure Solving Problem, University of Göttingen, Germany, 1986.
[14] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.
[15] K.W. Nordquest, D.W. Phelps, W.F. Little, D.J. Hodgson, J. Am. Chem. Soc. 98 (1976) 1104.
[16] P. Chaudhuri, M. Winter, U. Flörke, H.-J. Haupt, Inorg. Chim. Acta 232 (1995) 125.
[17] A.B.P. Lever, A. Mantovani, Inorg. Chem. 10 (1971) 817.
[18] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[19] C.C. Stoumpos, N. Lalioti, I.A. Gass, K. Gkotsis, A.A. Kitos, H. Sartzi, C.J. Milios, C.P. Raptopoulou, A. Terzis, E.K. Brechin, S.P. Perlepes, Polyhedron, in press, doi:10.1016/j.poly.2008.12.001.
[20] (a) S.P. Perlepes, E. Libby, W.E. Streib, K. Folting, G. Christou, Polyhedron 11 (1992) 923;
(b) J.-P. Costes, F. Dahan, J.-P. Laurent, Inorg. Chem. 24 (1985) 1018.
[21] A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[22] (a) H. Kwak, S.H. Lee, S.H. Kim, Y.M. Lee, B.K. Park, E.Y. Lee, Y.J. Lee, C. Kim, S.-J. Kim, Y. Kim, Polyhedron 27 (2008) 3484;
(b) A. Karmakar, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 1169.
[23] R.L. Rardin, W.B. Tolman, S.J. Lippard, New J. Chem. 15 (1991) 417.
[24] (a) C.B. Aakeröy, A.M. Beatty, D.S. Leinen, J. Am. Chem. Soc. 120 (1998) 7383;
(b) C.B. Aakeröy, A.M. Beatty, D.S. Leinen, K.R. Lorimer, Chem. Commun. (2000) 935.
[25] Q. Zhou, T.W. Hambley, B.J. Kennedy, P.A. Lay, P. Turner, B. Warwick, J.R. Biffin, H.L. Regtop, Inorg. Chem. 39 (2000) 3742.
[26] W. Clegg, I.R. Little, B.P. Straugham, J. Chem. Soc., Dalton Trans. (1986) 1283.
[27] R. Sharma, A. Karmakar, J.B. Baruah, Inorg. Chim. Acta 361 (2008) 2081.

[28] (a) H. Necefoglu, W. Clegg, A.J. Scott, Acta Crystallogr. E58 (2002) m121;
(b) V. Zelenak, M. Sabo, W. Massa, J. Cernak, Acta Crystallogr. C60 (2004) m85;
(c) T. Ohmura, W. Mori, T. Takei, T. Ikeda, A. Maeda, Mater. Sci. 23 (2005) 729.
[29] (a) T. Kawasaki, T. Kitazawa, Acta Crystallogr. E64 (2008) m788;
(b) B. Zhang, S. Chu, X. Wang, G. Shen, R.-J. Wang, Acta Crystallogr. E59 (2003) m824;
(c) C.B. Aakeroy, A.M. Beatty, D.S. Leinen, Angew. Chem. Int. Ed. 38 (1999) 1815;
(d) T. Kawasaki, C. Kachi-Terajima, T. Saito, T. Kitazawa, Bull. Chem. Soc. Jpn. 81 (2008) 268;
(e) A.M. Mutambi, Acta Crystallogr. E64 (2008) m979.