Synthesis and Structural Characterization of a Tetranuclear Zinc(II) Complex with *P,P′*-Diphenylmethylenediphosphinate (pcp) and 2,2′-Bipyridine (2,2′-bipy) Ligands

Andrea Ienco[a], Stefano Midollini[a], Annabella Orlandini[a], and Ferdinando Costantino[b]

[a] Istituto della Chimica dei Composti Organometallici, ICCOM-CNR, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy
[b] Dipartimento di chimica, università di Perugia, Via Elce di sotto 8, 06123 Perugia, Italy

Reprint requests to Dr. S. Midollini. Fax: +39-055-5225-203. E-mail: stefano.midollini@iccom.cnr.it

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A new tetranuclear complex of zinc(II) with *P,P′*-diphenylmethylenediphosphinate and 2,2′-bipyridine ligands was synthesized. [(pcp)(2,2′-bipy)Zn (μ_3-pcp)Zn (2,2′-bipy)]$_2 \cdot 6H_2O$ was characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis and X-ray diffractometry. The structure consists of tetranuclear complexes connected through water hydrogen-bonding interactions in corrugated 2D layers. Two crystallographically independent zinc ions are in a distorted five-coordinate environment, being surrounded by three oxygen atoms of phosphinate groups (from two pcp ligands) and by two bipy nitrogen donors. Of the two independent pcp anions the first one utilizes all of its oxygen donors to coordinate one metal as bidentate and two metal atoms as a monodentate ligand, whereas the second one is only bidentate for one metal atom.

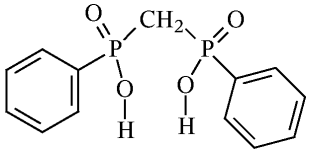
Key words: Zinc(II), Tetranuclear Complex, Diphosphinate, 2,2′-Bipyridine, Inorganic-Organic Hybrid

Introduction

Organic-inorganic hybrids constitute an important class of materials which because of their structural typologies are suitable for interesting applications in ion exchange, gas sorption, and catalysis *etc*. In this research area metal phosphonates or phosphinates have been found to be particularly versatile because they allow the introduction of a variety of organic groups into the hybrid structure [1 – 3].

Recently we have used P,P′diphenylmethylenediphosphinic acid (H_2pcp), shown in Scheme 1, to prepare a series of hybrid materials, with a variety of metal ions M(II) and structural arrangements (from 1D to 3D) [4 – 11]. In the case of zinc(II) we had success in the preparation of the unique complex [Zn(pcp)] which shows a two dimensional polymeric array, characterized by 2D layers built by strong coordinative linkages [9].

Now we report the synthesis and the structure of a new tetranuclear complex [(pcp)(2,2′-bipy)Zn (μ_3-pcp)Zn(2,2′-bipy)]$_2 \cdot 6H_2O$ which forms layers through a hydrogen bonding network. As far as we know the complex constitutes a unique example of a 2D zinc phosphinate cluster. Current interest continues



H_2pcp Scheme 1.

to revolve around the chemistry of Zn(II) ions associated with phosphate and related anions due their importance in biology [12 – 16]. In this context two unusual tetranuclear Zn(II) compounds containing bridging phosphite [17] or pyrophosphate [18] ligands have recently been reported.

Experimental Section

Chemicals were obtained from commercial sources and used without further purification. *P,P′*-Diphenylmethylenediphosphinic acid (H_2pcp) was prepared as previously described [19]. IR spectra of samples incorporated in a KBr disk were recorded on a Perkin-Elmer BX FT-IR spectrometer, in the 4000 – 400 cm^{-1} region. Coupled thermogravimetric (TG) and differential thermal (DTA) analysis were performed with a Netzsch STA490C thermoanalyzer under a 20 mL min^{-1} air flux with a heating rate of 10 °C min^{-1}.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{92}H_{92}N_8O_{22}P_8Zn_4$
Formula weight	2170.98
Temperature, K	293(2)
Wavelength, Å	1.54180
Crystal system, space group	triclinic, $P\bar{1}$
a, Å	16.851(4)
b, Å	14.718(10)
c, Å	10.867(14)
α, deg	78.07(9)
β, deg	79.36(3)
γ, deg	105.99(2)
Volume, Å^3	2450(4)
Z, calculated density, g · cm^{-3}	1, 1.472
Absorption coefficient, mm^{-1}	2.964
F(000), e	1116
Crystal size, mm^3	$0.475 \times 0.175 \times 0.10$
θ Range for data collection, deg	2.82 – 49.99
Limiting indices	$-16 \le h \le 16$, $-13 \le k \le 14$, $0 \le l \le 10$
Reflections collected / unique	6619 / 5033
Completeness to theta,%	100.0
Data / parameters	5033 / 604
Goodness-of-fit on F^2	1.049
Final R indices [$I \ge 2\sigma(I)$]	$R_1 = 0.0620$, $wR_2 = 0.1331$
R indices (all data)	$R_1 = 0.0797$, $wR_2 = 0.1447$
Largest diff. peak/hole, e · A^{-3}	0.852 / −0.414

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(3)	1.968(5)	P(1)–C(1)	1.803(8)
Zn(1)–O(6)	1.974(5)	P(2)–O(4)	1.494(5)
Zn(1)–O(1)	1.991(5)	P(2)–O(3)	1.513(5)
Zn(1)–N(2)	2.130(7)	P(2)–C(21)	1.797(9)
Zn(1)–N(1)	2.144(6)	P(2)–C(1)	1.818(8)
Zn(2)–O(8)$^{\#1}$	1.970(5)	P(3)–O(5)	1.497(5)
Zn(2)–O(5)	1.980(5)	P(3)–O(6)	1.499(5)
Zn(2)–O(7)	2.026(5)	P(3)–C(31)	1.792(8)
Zn(2)–N(4)	2.107(8)	P(3)–C(2)	1.828(7)
Zn(2)–N(3)	2.150(9)	P(4)–O(7)	1.495(5)
P(1)–O(2)	1.481(6)	P(4)–O(8)	1.505(5)
P(1)–O(1)	1.513(5)	P(4)–C(41)	1.805(8)
P(1)–C(11)	1.782(8)	P(4)–C(2)	1.806(7)
O(3)–Zn(1)–O(6)	106.2(2)	O(8)$^{\#1}$–Zn(2)–O(5)	116.9(2)
O(3)–Zn(1)–O(1)	96.6(2)	O(8)$^{\#1}$–Zn(2)–O(7)	97.9(2)
O(6)–Zn(1)–O(1)	98.6(2)	O(5)–Zn(2)–O(7)	92.7(2)
O(3)–Zn(1)–N(2)	137.2(2)	O(8)$^{\#1}$–Zn(2)–N(4)	110.6(2)
O(6)–Zn(1)–N(2)	114.9(2)	O(5)–Zn(2)–N(4)	131.8(3)
O(1)–Zn(1)–N(2)	89.0(2)	O(7)–Zn(2)–N(4)	88.7(3)
O(3)–Zn(1)–N(1)	91.2(2)	O(8)$^{\#1}$–Zn(2)–N(3)	96.0(3)
O(6)–Zn(1)–N(1)	93.7(2)	O(5)–Zn(2)–N(3)	91.5(3)
O(1)–Zn(1)–N(1)	163.1(2)	O(7)–Zn(2)–N(3)	161.8(4)
N(2)–Zn(1)–N(1)	75.2(3)	N(4)–Zn(2)–N(3)	75.4(4)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x$, $-y$, $1-z$.

*[(pcp)(2,2′-bipy)Zn(μ$_3$-pcp)Zn(2,2′-bipy)]$_2$ · 6H$_2$O (**1**)*

H_2pcp (40 mg, 0.135 mmol) and bipy (21 mg, 0.135 mmol) were dissolved in boiling water (50 mL) and then a solution of zinc acetate dihydrate (30 mg, 0.135 mmol) in water (10 mL) was added. The resulting solution was concentrated by evaporation in air, at *ca.* 90 °C, till colorless crystals precipitated. These were filtered, washed with water and dried in air, at r. t.

Yield 55 mg, 75 %. Alternatively the complex can be prepared by reaction of Zn(pcp) [9] with 2,2′-bipy in boiling water, and successive concentration of the solution at 90 °C.

$C_{92}H_{92}N_8O_{22}P_8Zn_4$: calcd. C 50.90, H 4.27, N 5.16; found C 50.97, H 4.35, N 5.20.

X-Ray crystallography

Diffraction data for the zinc derivative **1** were collected at r. t., on a Philips PW 1100 automatic diffractometer. Crystal data and data collection details of the structure are given in Table 1. The intensities I were assigned the standard deviations $\sigma(I)$ calculated by using a value of 0.03 for the instability factor k [20]. They were corrected for Lorentz and polarization effects and an empirical absorption correction was applied [21]. Atomic scattering factors for neutral atoms were taken from ref. [22]. Both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms [23]. The structure was solved by Direct Methods

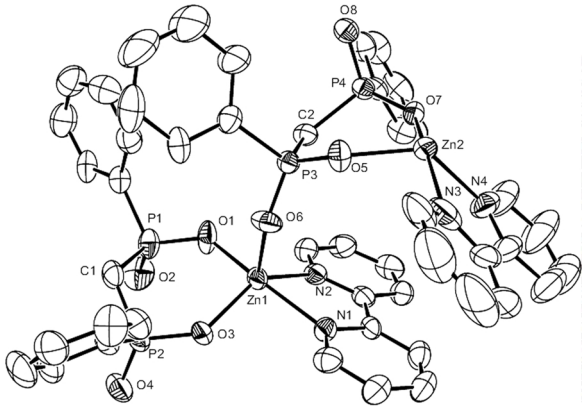


Fig. 1. Asymmetric unit of the structure of **1**, omitting solvent water molecules. ORTEP drawing with 30 % probability ellipsoids.

and refined by full-matrix least-squares methods on F^2, with anisotropic thermal parameters assigned to all non-hydrogen atoms. The hydrogen atoms were introduced in calculated positions riding on their carbon atoms, with thermal parameters 20 % larger than those of the respective carbon atoms. The function minimized during the refinement was $\Sigma w(F_o^2 - F_c^2)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 11.78P]$ ($P = (\max(F_o^2, 0) + 2F_c^2)/3$). All calculations were performed on a Pentium processor, using the package WINGX [24] (SIR97 [25], SHELX-97 [26], ORTEP-III [27]).

CCDC 646347 contains the supplementary crystallographic data for this paper. These data can be obtained free

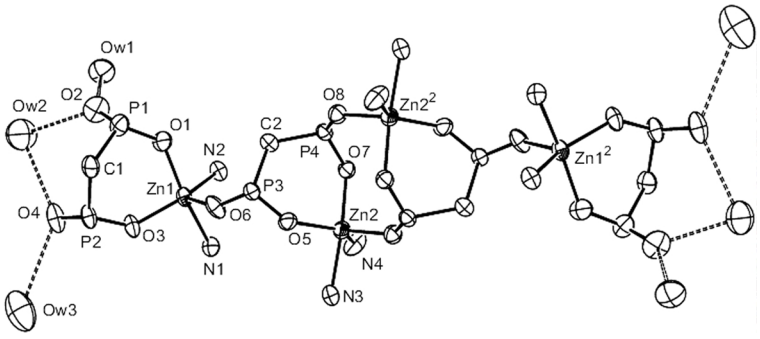


Fig. 2. Complete connectivity pattern of the tetranuclear complex. Phenyl rings and 2,2′bipy's carbon atoms are omitted for clarity. Superscript 2 refers to the symmetry operation: $-x, -y, -z$.

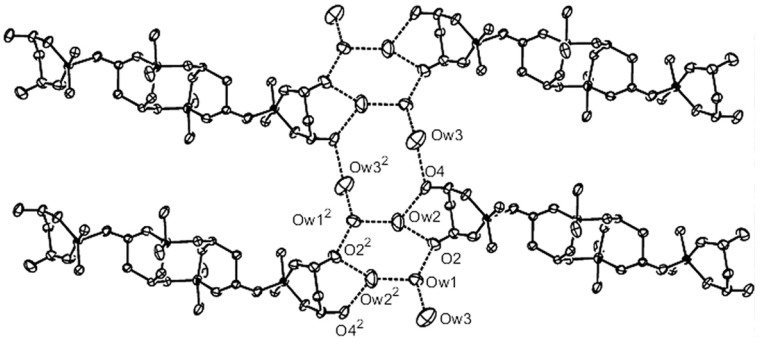


Fig. 3. A layer built up by tetranuclear units connected through the hydrogen bonding network of the water molecules. Phenyl rings and bipy's carbon atoms are omitted. Superscript 2 refers to the symmetry operation $-x, -y, -z$.

of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The reaction of zinc(II) acetate dihydrate with H_2pcp in the presence of 2,2′-bipy in water solution at 80 – 90 °C allows the isolation of colorless crystals of the title complex. Alternatively the compound can be obtained through the reaction of the otherwise insoluble polymer Zn(pcp) [9] with 2,2′-bipy in boiling water. The IR spectrum of the product, with a strong broad band in the OH stretching vibration region (*ca.* 3400 cm^{-1}), indicates the presence of water molecules.

The structure consists of tetranuclear complexes [(pcp)(2,2′-bipy)Zn(μ_3-pcp)Zn(2,2′-bipy)]$_2 \cdot 6H_2O$ (hereafter **1**), connected through water hydrogen-bonding interactions into corrugated 2D layers. Selected bond lengths and angles are given in Table 2. In the asymmetric unit of **1** there are two zinc(II) metal ions, two pcp and two 2,2′-bipy ligands and three water molecules. Figs. 1 and 2 show the asymmetric unit (except for the solvent molecules) and the complete connectivity of the tetranuclear complex, respectively.

In the tetranuclear complex, which lies on a center of symmetry, the Zn centers are linked by pcp bridging ligands. The two crystallographically independent zinc ions present analogous five-coordination polyhedra, as each metal is surrounded by three phoshinate oxygen atoms (from two pcp ligands) and two nitrogen donors (from one 2,2′-bipy). The coordination geometry is intermediate between trigonal bipyramidal and square pyramidal, with τ factors (= 1 for ideal trigonal bipyramidal and 0 for ideal square pyramidal) reaching the values of 0.43 and 0.50 for Zn1 and Zn2, respectively. The two independent pcp anions act differently, as the central one utilizes all of its oxygen donor atoms to coordinate one metal cation as a bidentate and two cations as a monodentate ligand, whereas the terminal one chelates only one cation, and engages the free oxygen atoms in hydrogen bonding with water molecules. The water molecules create a network of hydrogen bonds, which connect the tetrameric units into a corrugated 2D layer (Fig. 3). The most important linkages are as follows (Å): O2···O1w 2.802; O2···O2w 2.643; O4···O2w 3.034; O4···O3w 3.289; O1w···O2w(I) (I = $1-x, -1-y, 1+z$) 2.788; O1w···O3w(II) (II = $x, y, z-1$) 2.822.

While Zn1 participates in one six-membered ring, which is generally formed upon the chelation with the

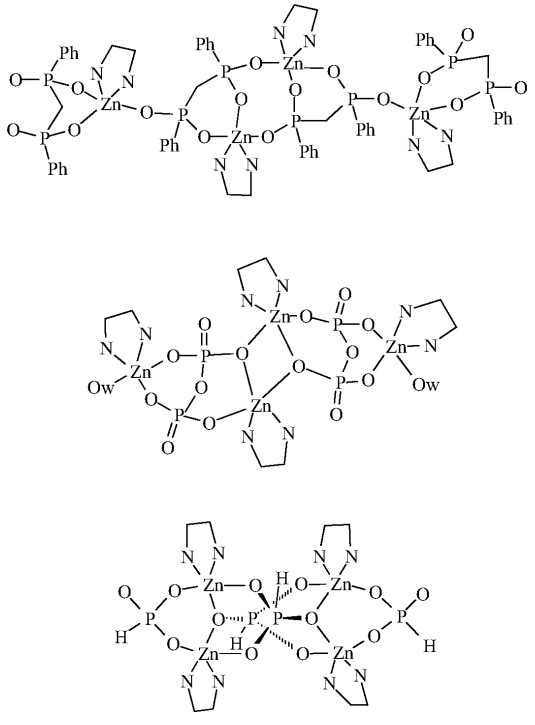


Fig. 4. Schematic drawings of the tetranuclear complexes [(pcp)(2,2′-bipy)Zn-(μ_3-pcp)Zn(2,2′-bipy)]$_2$ (**1**), [(2,2′-bipy)Zn(H_2O)(μ_3-P_2O_7)Zn(2,2′-bipy)]$_2$ (**2**) [18] and [(2,2′-bipy)Zn(HPO_3)]$_4$ (**3**) [17].

pcp ligand, Zn2 is part also of an eight-membered ring, which has a pseudo-chair conformation. The same eight-membered ring, formed by zinc cations and phosphinate anions in an alternating array, has been reported in the related Zn/pcp hybrid complex [9], which presents a 2D layer structure, featuring a mesh-net. Bond lengths and angles in both zinc coordination spheres are very similar, and in agreement with literature data. As concerns the P–O bond lengths, those involved in coordination [P(1)–O(1), P(1)–O(3), P(2)–O(5), P(2)–O(7) (av. 1.505(5) Å)] are slightly larger than those of the phosphoryl P–O groups [P(1)–O(2), P(2)–O(4), P(3)–O(6), P(4)–O(8) (av. 1.494(5) Å)] as expected.

It appears of interest to compare the structure of **1** with that of the tetranuclear clusters in [(2,2′-bipy)Zn(H_2O)(μ_3-P_2O_7)Zn(2,2′-bipy)]$_2 \cdot 14H_2O$ (**2**) [18] and [(2,2′-bipy)Zn(HPO_3)]$_4$ (**3**) [17]. Schematic drawings of the three tetranuclear clusters are shown in Fig. 4. In all three clusters the four Zn(II) ions, chelated by 2,2′-bipy, are cemented together by the bridging phosphorylate anions (μ_3-diphosphinates in **1**, μ_3-pyrophosphates in **2**, or μ_4- and μ_2-phosphites in **3**). Each cluster contains two crystallographically independent Zn atoms whose coordination geometries (N_2O_3 donor atoms sets) range from TBP (**2**) to intermediate between TBP and SP (**1**), and SP (**3**). These structural arrangements occur through the formation of six- and eight-membered (**1** and **3**) or four- and six-membered chelate rings (**2**). Whereas in **2** and **3** some oxygen atoms are in bridging positions between two metal atoms, in **1** all the coordinated oxygen atoms bind only one zinc atom; this peculiar feature of **1** has to be related to the space needed by the phenyl groups of the diphosphinate ligands.

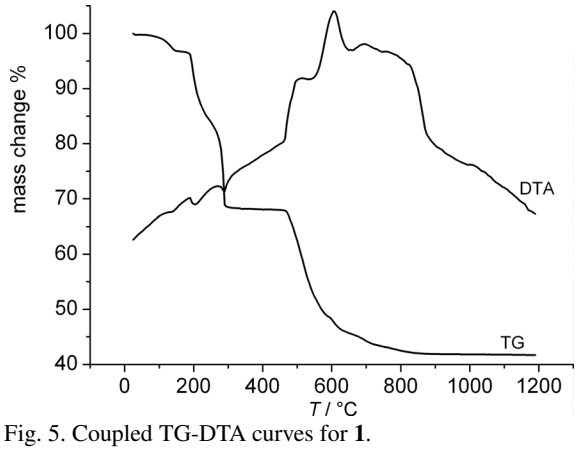


Fig. 5. Coupled TG-DTA curves for **1**.

The thermal behavior of complex **1** has been investigated in the temperature range 25 – 1200 °C. The coupled TG-DTA curve is shown in Fig. 5.

The first weight loss (4.5 %) starts at about 100 °C (up to 150 °C) and corresponds to the loss of the six water molecules (calcd. 4.97 %). This relatively high temperature is consistent with the fact that the water molecules are strongly involved in a complicated hydrogen-bonding network and anchored to the structural scaffold.

The second weight loss (28 %) is observed between 200 and 280 °C and corresponds to the loss of the 4 molecules of 2,2′-bipy per mole of compound (calcd. 28.5 %). This weight loss is related to an endothermic reaction as observed in the DTA curve, and it could mean that bipy evaporates from the solid without combustion. Subsequently a plateau is observed between 280 °C and 510 °C which appears to correspond to the formation of the stable Zn(pcp) phase.

The last weight loss (30 %) is observed up to 1000 °C, related to the combustion of the organic part of the pcp ligand. At the end of the analysis only a mixture of $Zn_2P_2O_7$ and ZnO was left.

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